

## Ligand Based Soil Extraction Geochemistry

Mann, A. W. <sup>[1]</sup>

1. MMI Technology, Bentley, Western Australia

### ABSTRACT

*Ligand based soil extraction geochemistry is a high resolution, multi-element soil analysis technique for mineral exploration. The use of strong complexing ligands in the extraction procedure limits matrix element interference, reduces background analyte values (noise) and overcomes potential pH effects. Improvements in the spatial and amplitude (signal to noise) resolution of this technique compared to total digestion or more aggressive partial digestions is useful not only in areas with exotic cover, but in residual and weathered terrain where duricrust development and mechanical transport can cause dispersion of anomalies. At the Green Tree Frog Prospect in Queensland, Australia superior amplitude contrast and more accurate delineation of sub-surface mineralization is observed for ligand based geochemistry compared to fire assay in terrain with exotic tertiary cover. In Guinea, West Africa ligand based soil extraction of gold has outlined five new economic zones since its introduction. Comparison of a range of partial digestions and extractions from glacial till at Cross Lake, a VMS deposit in the Abitibi belt of Canada, provides very strong evidence of the value of a strong ligand in the extraction. More recent developments of this technique utilise compatible and incompatible elements (principally Ce and Ni) to obtain inferred geology images, which are of direct assistance to exploration where outcrop and sub-crop is limited or of low density. A prospect scale image of inferred geology from The Mount SE, Widgiemooltha in the Eastern Goldfields of the Yilgarn Craton, Western Australia obtained from a ligand based soil geochemistry program provides superior (and Ni exploration-pertinent) detail to 1:40,000 standard geological mapping. A semi-regional scale roadside sampling program at Wongan Hills on the western side of the Yilgarn Craton illustrates that this type of geochemistry has a role to play in early-stage, regional scale exploration where geological outcrop and sub-crop is limited.*

### INTRODUCTION

Increasingly, mineral exploration is being undertaken in areas with greater soil coverage and less geological exposure. The challenges of exploring effectively in such areas have in the last decade tended to rely heavily on geophysical and other remote sensing techniques. Whereas many new and innovative advances have been made with these techniques, it is the opinion of many exploration geologists that advances in geochemical techniques have by comparison been relatively limited over the same time frame. They are however, far from non-existent. For example, improvements to Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) in sensitivity, accuracy and reliability have seen application of this technique bring significant advancements to soil geochemical prospecting methods (Caughlin, 2007). Along with this we have seen a revitalization of partial or selective extraction techniques which are ideally suited to this instrumentation and enable it to fully utilize the inherent low detection limit capabilities.

This paper will explore one such technique using a new and different approach— ligand-based soil extraction geochemistry, which has been commercially available for over a decade and used currently for mineral exploration around the world, in a range of terrain types, for a number of different commodities.

One important reason why such techniques have come to the fore is that a great limiting factor – relatively high instrument detection limits – which prevailed when partial digestion

geochemistry was first developed in the last half of the previous century, are no longer a factor. For most elements the lower limit of detection on ICP-MS after partial digestion of soils from most terrain types is now below natural background levels. The use of partial extractions reduces the amount of spectral background from unwanted or matrix-type analytes such as iron, silica, manganese and aluminum which cause many interferences or at best raise lower detection limits. More importantly, partial digestions and extractions appear to have the ability to discriminate in favour of the “active” ionic (source-related) signature of required commodity and pathfinder elements, relative to their “geochemical background” or mechanically transported signature, thereby improving both spatial and amplitude resolution of anomaly signals. This is the chemical equivalent of a geophysical technique which has improved resolution by filtering out unwanted “noise”.

In this paper, the methods of achieving improved resolution, the consequences of this, and some case histories are presented. Concepts and methodology behind a relatively new application for multi-element soil geochemistry – inferred geology - are also included along with two examples from the Yilgarn Craton Western Australia.

## METHODS

### Partial Digestion and Extraction Techniques

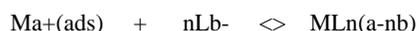
The distinction between a partial digestion and partial extraction is a technically important one that needs to be made clear to avoid confusion and mis-representation. A partial digestion is one in which part of the soil matrix is dissolved (as opposed to conventional or total digestion where the entire soil sample is dissolved). It can be either selective or non-selective. In the case of a selective partial digestion, it is the aim of the digesting solution to dissolve preferentially one of the soil phases (e.g. amorphous iron oxide or organics), whereas a non-selective digest dissolves some of several or all matrix phases along with their contained or adsorbed elements. However as succinctly pointed out by Chao (1984) "Any claim that individual components can be isolated by partial dissolution techniques, and that metals released into the extract are genetically related to individual components, should be viewed with reservation".

By contrast a partial extraction attempts to dissolve or detach analytes from the soil matrix without dissolution of the matrix. Again, and by analogy with Chao's comment above, it is probably not possible to completely and successfully achieve this, and some small component of at least one phase will usually be dissolved. It is however one of the primary aims of this geochemical method to achieve dissolution of particularly the adsorbed elements, many of them metals, without significantly dissolving the substrate to which they are attached. Thus bound material or metals occluded or included within the matrix will in general not be dissolved. In general the stronger the digestion, the greater the dissolved analyte concentrations and the lower the contrast. The converse is also true – up to a point. Whilst weaker digestions/extractions produce greater contrast there must be sufficient complexing strength to ensure reproducibility in the procedure. Distilled water for example will dissolve some elements from soils to provide the ultimate "weak leach", but it is restricted to very soluble elements and is irreproducible analytically due to re-adsorption.

Non-selective partial digestions, are generally based on mineral acids or mixtures thereof. Table 1 shows some examples of selective and non-selective digestions, as well as some examples of the alternative method – partial extraction.

### Ligand Based Soil Extractions

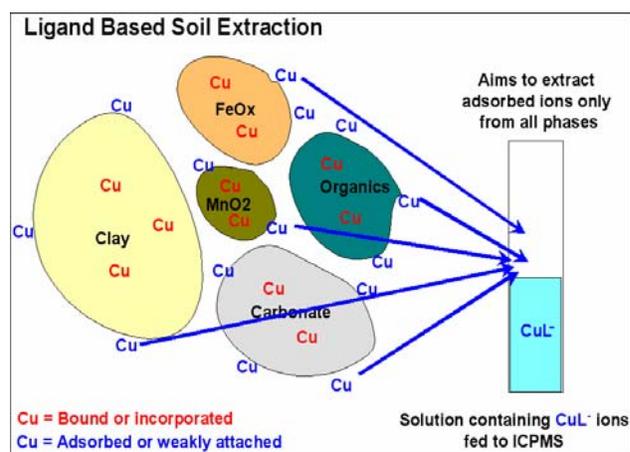
One way of achieving adsorbed metal dissolution whilst minimizing problems of re-adsorption is to have the extracting solution contain a strong ligand for each analyte that is capable of complexing with and detaching adsorbed ions and converting them to soluble species. A ligand is simply an inorganic or organic species that has strong complexing affinity for the analyte. Thus if the analyte is the metal species  $Ma^{+}(ads)$ , and the ligand is represented by species  $Lb^{-}$  then the desorption or dissolution reaction can be written:



The dissolved species  $MLn$  can have positive, zero or negative charge depending on the number of complexing anions, which is dependent on the coordination chemistry of the central cation. It is a requirement for effective soil extraction that each analyte  $M$  has an excess of its strong ligand  $L$  in the extraction solution. Some ligands can complex a number of metals but in general metal-ligand chemistry is very specific, and for multi-element extraction a range of ligands is required. Most metals have more than one possible complexing ligand. Figure 1 shows schematically the dissolution process for copper. Note that the number of adsorbed ions that are desorbed is determined by ligand strength and bonding energy status – partial extractions are operationally defined.

**Table 1: Examples of soil digestion and soil extraction solutions.**

	DIGESTIONS	
Selective	Selected Phases	Non-selective (attacks all phases)
Ammonium Oxalate	Amorphous iron oxide	Dilute Nitric Acid
Hydroxylamine	Mn+Fe Oxides	Dilute Hydrochloric Acid
Hydrogen peroxide	Manganese Oxides	Sodium Hydroxide
Enzyme Leach	Manganese Oxides	Aqua regia
Sodium Hypochlorite	Organics	
Acid acetates	Carbonates	
Selective	EXTRACTIONS (from selected phases)	(extraction from all phases)
EDTA	Amorphous iron oxides	Magnesium Chloride
Sodium Pyrophosphate	Organics	Ammonium Acetate
		BLEG
		MMI (A,B, M)



**Figure 1: Schematic of ligand-based soil extraction geochemistry.**

Most analytes of interest have values in the range 0.1ppb to tens of ppm in solution after extraction from a soil, depending on the analyte and depending on whether or not the soil is a background sample or over an anomalous zone for that analyte. It is the function of the ligand to accommodate all analytes which complex or chelate with it. It must have a concentration in solution considerably higher than that of the analytes. Re-adsorption of the analyte is an important problem which confronts any partial or weak digestion or extraction (Hall, 1998). The presence of a strong ligand will assist in maintaining the analyte in solution during the analytical process (e.g. Gray et al, 1998).

The effects of chelating ligands in solution on analytes is profound – much more important than for example the effects of pH. It is well known (e.g. Mann & Deutscher (1977), Mann and Deutscher (1980)) that base metals have limited solubility in normal aqueous solutions in the pH range 6-9. As shown in Figure 2, for Cu this results in a solubility of approximately 60ppb at pH 8, due primarily to the precipitation of insoluble hydroxy-carbonates. The copper insolubility area is shown in red (multiple curves indicate the (small) effect of weak ligands), the operating range for copper soil extractions is shown in green.

Without a strong ligand, the operation of an extraction solution is clearly compromised in the pH range 6-9. The addition of a strong ligand for copper changes this situation - it increases the solubility of copper by several orders of magnitude. Cyanide is just one ligand which will produce this effect for copper –high copper concentrations in gold-cyanide circuits even in the presence of carbonate are testimony to this fact. The effect on the solubility curve for copper can be illustrated schematically as in Figure 3.

The solubility curve for copper has been raised by several orders of magnitude – to well above the operating concentration range for soil extractions by the complexing of copper ion with the ligand. This is easily demonstrated; 1,000ppm Cu in solution will have an intense blue colour. This is maintained even in the presence of calcium carbonate if and only if the solution contains a strong ligand for Cu. These chemical principles also influence adsorbed Cu, as evidenced by field results from soils containing carbonates e.g. caliches in Mexico. Anomalous values of Cu are observed in pH neutral strong ligand extractions of these carbonate soils where sources have provided sufficient Cu to penetrate and permeate caliche layers. An extraction solution with a pH in the range 6-9 is entirely suitable for extraction of base metals provided it contains high concentrations of suitable complexing ligands. It is not necessary to strongly buffer pH. Whilst difficult, it is possible, with suitable choice of multiple ligands, to prepare an extractant which will extract over 40 elements simultaneously, over very different concentration ranges. Table 2 shows the lower detection limits for 44 elements which can be obtained from a commercially available ligand-based extractant.

Figures 4(a) and 4(b) show that repeatability is good for two elements with very different concentration ranges, and different ligand requirements.

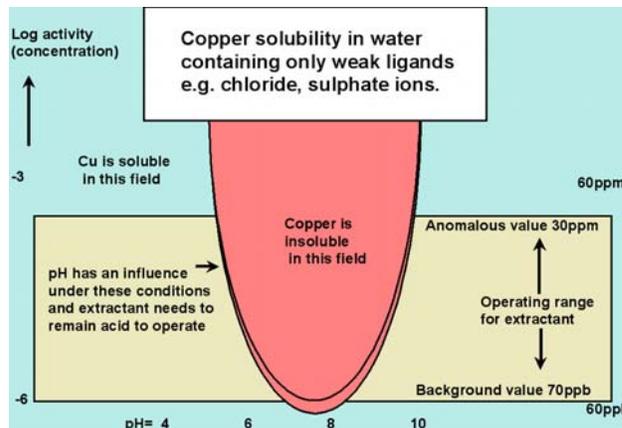


Figure 2: Solubility curve for copper in aqueous solution containing only weak ligands such as chloride and sulphate ions. (After Mann & Deutscher (1977)).

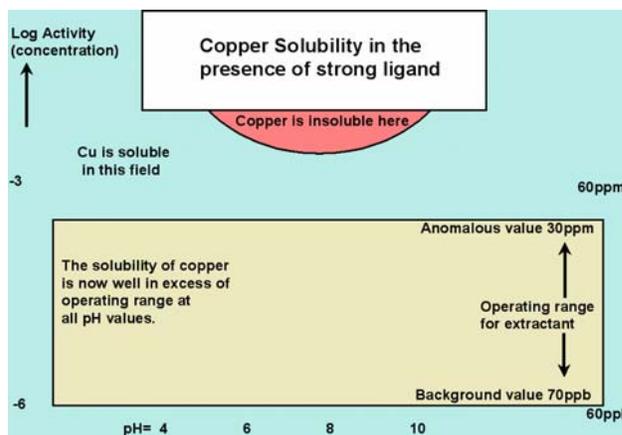
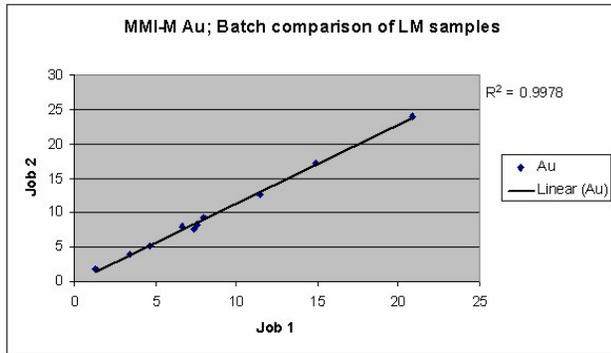


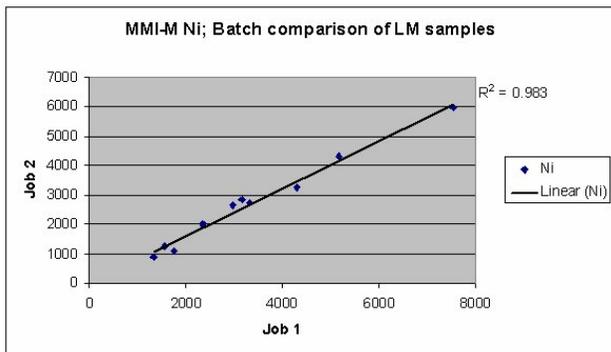
Figure 3: Effect of a strong ligand on the solubility curve for copper.

Table 2: Lower detection limits in ppb for elements available from a commercially-available ligand-based extraction (MMI-M).

Elem.	LDL	Elem.	LDL	Elem.	LDL	Elem.	LDL
Ag	0.1	Cu	10	Ni	3	Tb	0.1
Al	100	Er	0.1	Pb	10	Te	1
As	1	Fe	100	Pd	0.1	Th	1
Au	0.1	Gd	0.1	Pr	0.1	Ti	10
Ba	10	La	0.1	Rb	5	Tl	10
Bi	3	Li	0.2	Sb	0.1	U	1
Ca	200	Mg	10	Sc	1	W	0.2
Cd	1	Mn	10	Sm	0.1	Y	0.1
Ce	0.1	Mo	5	Sn	2	Yb	0.1
Co	0.3	Nb	0.1	Sr	10	Zn	20
Cr	1	Nd	0.1	Ta	200	Zr	1



**Figure 4(a):** Repeat analysis of Au, from a commercially available multi-ligand extraction.



**Figure 4(b):** Repeat analysis of Ni, from a commercially available multi-ligand extraction.

The sampling requirements are very simple. It has been found by experimentation and field experience (e.g. Mann et al, 2005) that the adsorbed ions are predominant in near-surface (or true soil interface if covered with organic matter) horizons. This is where evapo-transpiration is a maximum and capillary rise terminates – typically 10-25cm below the surface (interface). No processing of the soil is required apart from coarse sieving. If all soil samples in a survey are treated with an equivalent strong ligand containing solution they will reflect faithfully differences in adsorbed concentrations of analytes across the survey area. In such circumstances it is logical to conclude that differences in analyte concentrations in the soil are a result of natural processes which can be potentially related to a source.

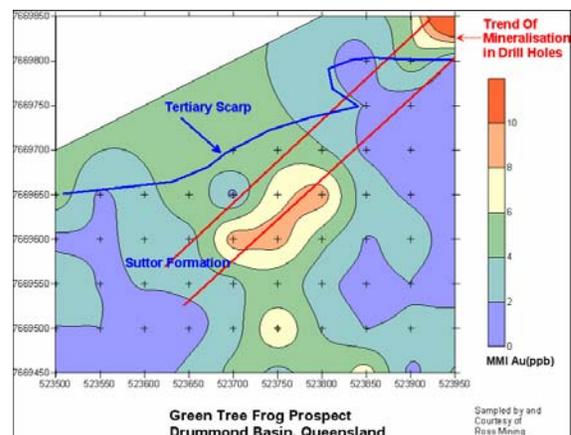
**CASE HISTORIES**

**Green Tree Frog Prospect, Queensland , Australia**

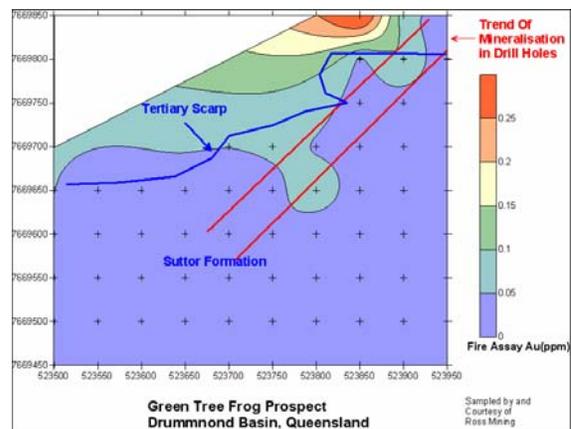
In this first case history the results for Au from a ligand-based soil extraction and a total soil extraction (fire assay) are compared. The known trend of mineralisation, from a series of drill holes is shown on both diagrams in Figure 5 (after Mann et al, 2000).

This case history demonstrates several important features of ligand-based soil extractions. The mineralisation lies beneath 20m of tertiary cover, the Sutor Formation in Queensland, Australia. Firstly, both techniques show similar but not identical

images. There is a relationship between them; the ligand-based extraction has not necessarily produced new anomalies but given better resolution. Secondly, although the absolute concentration of gold after ligand-based extraction is much lower, the amount of detail is much greater. This is because the fire assay has included a great deal of “bound” gold that has spread and displaced the anomaly. In essence this is due to the fact much of the dissolved gold has spent a great deal of time in the near surface and as a result has been mechanically dispersed from where it first was implanted, thus confusing the picture. By contrast the gold adsorbed onto soil particles and extracted into the ligand-based extraction solution is recent, not yet incorporated into soil forming processes and more closely related to source. For this reason partial soil digestions which dissolve a particular phase of the soil, if it contains both bound and as well as adsorbed analyte, will not be as well resolved as those containing only adsorbed ions from partial extraction. Another way to express this is to use the anomaly to background ratio, or response ratio. In the example above, the anomaly (in the north eastern corner) is twenty nine times background for the ligand-based soil extraction and less than ten times background for the fire assay. Soil digestion techniques such as aqua regia digestion will usually have a response slightly superior or equivalent to total digestion but inferior to partial extraction due to their inherent dissolution characteristics.



**Figure 5(a):** Soil survey for Au after ligand based extraction.

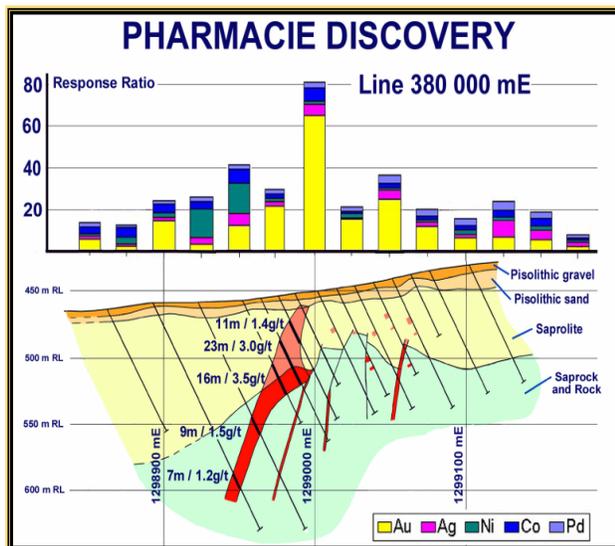


**Figure 5(b):** Soil survey after fire assay of soil samples.

The resolution above is also improved spatially as well as in amplitude (relative to background). Even where the tertiary cover is absent in the northeast corner of the survey area, the maximum response for the total digestion method is down-slope from both the partial extraction soil maximum and the trace of mineralisation – a sure sign of mechanical transport. Increased resolution is not just useful in covered terrain but is effective also where the regolith is residual or erosional. If the purpose of executing a soil survey is to define and optimise drilling locations, a 100m displacement (as in this case) can be the difference between success and failure.

**LEFA Gold Corridor, Guinea, West Africa**

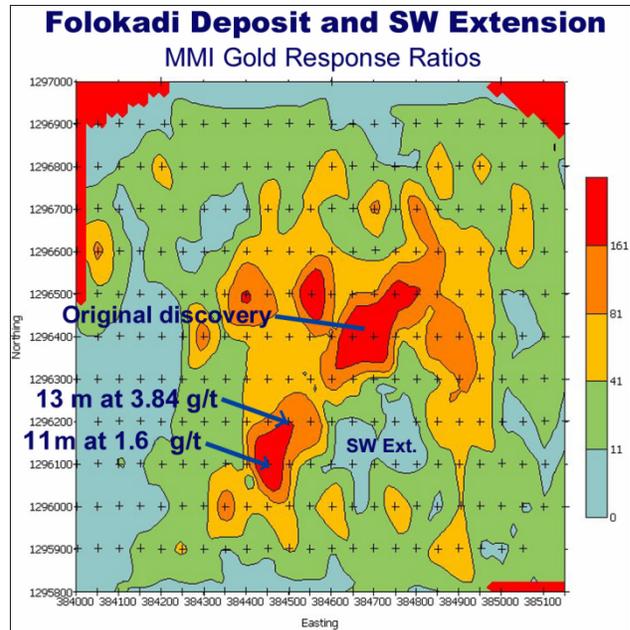
The second case history, from Africa illustrates the usefulness of high resolution geochemistry derived from ligand-based soil extraction geochemistry in residual terrain. Lateritic terrain, particularly where the surface consists of pisolitic gravels, contains significant gold, but such gold is widely dispersed because of mechanical processes. Targeting mineralisation, often residing beneath an extensively weathered saprolite zone is difficult. In the Pharmacie area of the LEFA Corridor, conventional geochemistry defined a broad area with anomalous values but extensive drilling failed to locate a source. Following the introduction of a ligand-based soil extraction method, a “new” anomalous area was highlighted within the broad zone. Results for one section are shown in Figure 6.



**Figure 6:** Multi-element response from a ligand based soil extraction program across gold-containing weathered residual terrain, West Africa. (Courtesy Kenor, B. Varndell, P. Mc Mickan, Lithofire)

The first line of drilling subsequent to and based on the ligand-based geochemistry intersected mineralisation.

A survey using the same ligand-based extraction technique was used to cover both the area of the known Folokadi deposit and beyond its known boundaries (Figure 7).



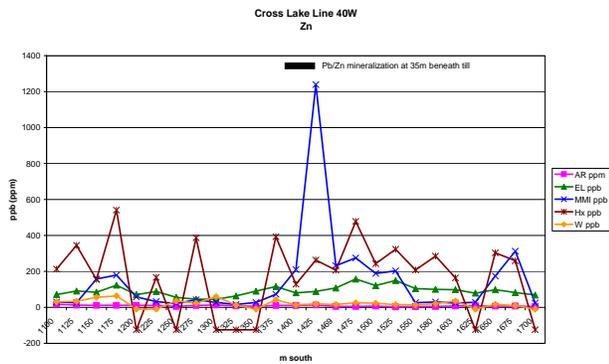
**Figure 7:** Ligand-based soil extraction program, vicinity Folokadi deposit. (Courtesy B. Varndell, P. McMickan, Lithofire).

The known Folokadi deposit was clearly delineated. In addition a south western extension was also outlined. In this gold camp, which by March 2005 contained proved and probable reserves of 2.3 million ounces (40.5Mt @ 1.7g/t Au), ligand-based extraction geochemistry operating within the ferricrete (cuirasse) outlined five new economic gold zones. Significantly a large amount of RAB drilling to locate them was eliminated.

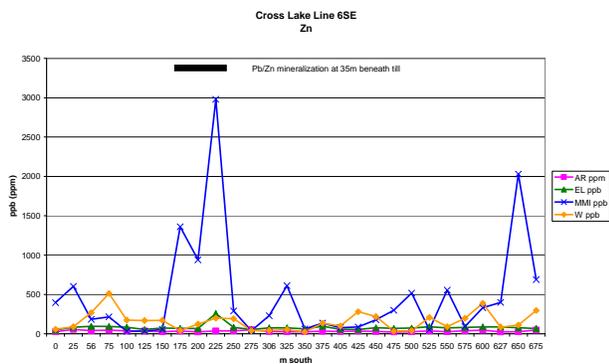
**Cross Lake, Abitibi, Canada**

In 1999 and 2000 an industry sponsored CAMIRO study was undertaken the purpose of which was to compare the efficacy of different partial digestions and extractions at several mineralised sites in different geological and climatic settings. One of the sites chosen was at Cross Lake, which hosts Cu, Zn +/-Pb VMS-style mineralization located under 30-50m of exotic (till, glacial outwash gravel, sand and lacustrine clay) overburden in the Abitibi belt of Canada (Hamilton et al, 2001). Two lines of samples were taken in 1999, 40E and 6SE. On the former line the water table was approximately 2m below surface, on the latter less than 1.5m and sometimes artesian. Topographically the area is gently sloping, and forested with spruce, alder, fir and jack pine. Soil samples in 1999 for most techniques were taken from the B horizon whilst MMI samples were taken strictly from 10-25cm below the Ao horizon, which was used as the datum.

Figures 8(a) and 8(b) show the Zn values obtained from the samples on these two lines.



**Figure 8(a):** Line 40W Cross Lake. Zn values obtained from aqua regia (AR), Enzyme Leach (EL), Mobile Metal Ion (MMI), hydroxylamine in 0.1M nitric acid (Hx) and water (W) Leaches. The units (ppb or ppm) are shown in the legend.



**Figure 8(b):** Line 6SE Cross Lake. Zn values obtained from aqua regia (AR), Enzyme Leach (EL), Mobile Metal Ion (MMI) and water (W) leaches. The units (ppb or ppm) are shown in the legend.

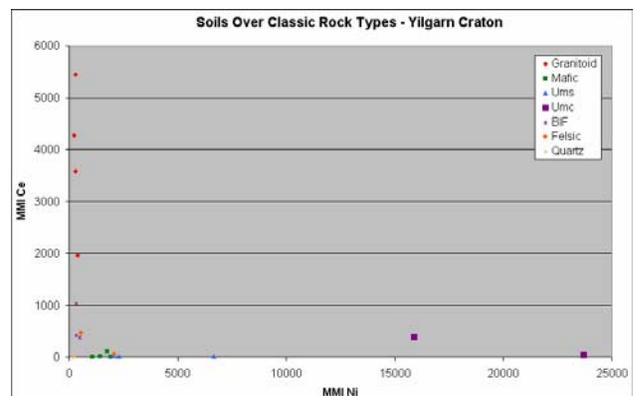
Initially, some of the differences observed were ascribed to differences in sampling depth in the 1999 survey. Careful examination of the depth data however shows that for over 50% of sites, samples were taken from similar depths (i.e. the B horizon was close to 10-25cm below datum). Importantly, the crucial and anomalous samples over mineralization at 1425S on Line 40W and 225S on Line 6SE were taken at the same depth (10-25cm below datum) for all techniques. In Figures 8(a) and 8(b) the aqua regia extractions show overall higher concentrations of Zn (values are in ppm), but little or no contrast over the mineralization (i.e. background values are also high). Enzyme Leach, a weak peroxide based leach indicates a small peak over mineralization on line 6SE but none on line 40W. Water shows low extraction values for Zn. By contrast, MMI, the only strong ligand based extraction, shows significant contrast over mineralization on both lines (the subsidiary peak at the southern end of both lines was subsequently proved by drilling to be over similar (weakly mineralized) lithology to the VMS deposit). Re-sampling in 2000 with all samples at the same depth (10-25cm) at all sites produced similar (strong contrast) results for MMI and weaker but significant responses for Enzyme Leach and an ammonium acetate leach (H. de Souza, pers. comm.). These results suggest that a greater proportion of the Zn directly attributable to the deposit resides in

an adsorbed form which has been made soluble by the strong ligand. Conversely much of the background Zn which is less directly linked to mineralization, and which has been re-worked by mechanical processes over time, resides internally within soil phases and is only released by strong digestion solutions.

### INFERRED GEOLOGY

Obtaining reliable bedrock geological information is also one of the challenges facing mineral exploration in areas with deep overburden and/or exotic cover. The Yilgarn Craton of Western Australia consists of a series of greenstone belts comprising mafics, ultramafics, felsics and sediments interspersed in granitoid terrain. Exposure is relatively good in parts of the western margin and in the Eastern Goldfields, but large areas are covered with colluvium and alluvium. Weathering is almost ubiquitous, sometimes to depths of 80m, and even where outcrop is available weathering can make correct interpretation of rock types difficult.

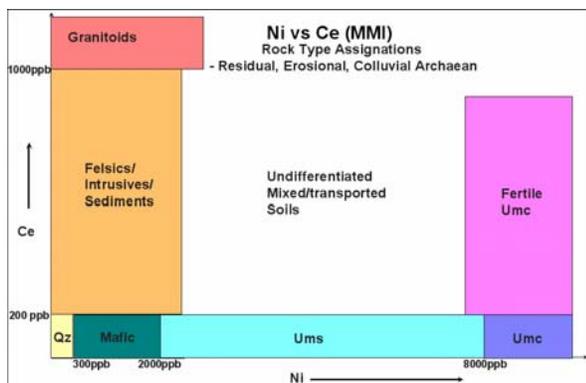
As a first step to applying multi-element soil geochemistry to bedrock identification, a small number of selected outcrops in the Eastern Goldfields, and on the western edge of the Craton were chosen, where rock outcrop was evident, the rock type known, and uncontaminated soil available. Soils were taken from near large areas of outcrop, and upslope to avoid any potential problems with mechanical dispersion or mixing. The soils over these "classic" rock sites were analysed for over 30 elements. The method is predicated on the fact that the extraction solution has ligands which are capable of complexing with these elements. A plot of Ce vs. Ni is shown in Figure 9.



**Figure 9:** Plot of Ce versus Ni for soils over "classic" rock sites on the Yilgarn Craton.

It is immediately apparent that soils over mafic and sheet flow and channel flow ultramafic rocks (Ums and Umc) plot along the x axis (i.e. have low Ce) whilst felsics, sediments (Banded Iron Formation - BIF) and granitoids plot along the y axis (i.e. have low Ni). Nickel is a "compatible" element commonly found in mafic and ultramafic melts. Cerium on the other hand is one of many "incompatible elements" whose large ionic radius causes it to be incorporated into crystals late in a differentiating magmatic sequence. Cerium is found in high concentrations in granitoids, but also in felsic rocks and some sediments.

Conceptually, at least for soils over a single rock type, this leads to the conclusion that particular areas or zones of the Ni versus Ce diagram can be used to infer the likely underlying rock type, based solely on the soil analysis. This can be schematically represented as shown in Figure 10.



**Figure 10:** Schematic representation of underlying rock types based on Ni and Ce soil analysis.

It is a relatively simple matter, in the Excel spreadsheet of soil analysis results, (using IF/AND statements) to assign upper and lower limits to the “boxes” of Figure 10, and derive probable inferred rock types, initially based on Ni and Ce values in the soil analysis. Each assigned rock type can be given a discrete coded number for imaging, or each discrete rock type can be assigned a column in the Excel spreadsheet which is coded with a zero or unity for later plotting and overlay. For example, a soil with over 1000ppb Ce and less than 2500ppb Ni is likely to be granitoid in origin. Soils with less than 1000ppb Ce and 2500ppb Ni are likely to be felsic or sediments; using just Ce and Ni it is not possible to distinguish these, and other elements e.g. Ca, Fe and/or Ti need to be used. Soils with very low Ce and Ni are likely to be derived from quartz (or sandstones), whilst mafics have low Ce and Ni in the range 300-2000ppb in residual soils. Above 2000ppb Ni and Ce less than 50ppb is suggestive of sheet flow ultramafics (Umc), and above 7000-8000ppb Ni has been shown to closely correlate with channel flow or accumulate ultramafics (Umc) (Mann et al, 1995). It will be noticed that there is a special but relatively rare category (fertile Umc) on Figure 10. This is to accommodate bases of cumulate ultramafics which have made thermal contact with, and assimilated felsic fragments and Ce (and S). These rocks are potential host horizons for NiS deposits, and their geochemistry is reflected in the soil geochemistry (i.e. they have both very high Ni and appreciable Ce) (Hill (2001)).

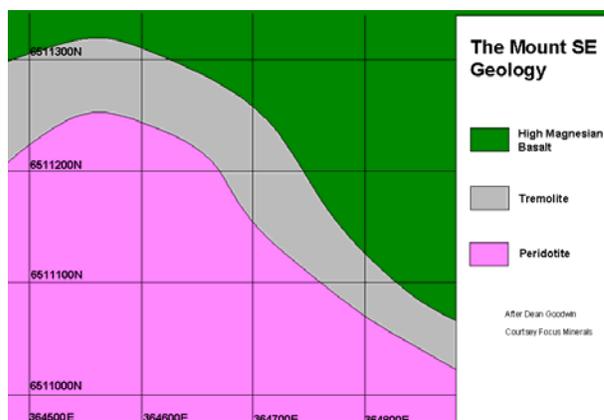
It is of note that the above scheme has been predicated on (and should strictly apply to) unmixed or pure soils of residual origin. As will be shown in the following examples this extends to weathered erosional soils and colluvium without modification, and to some mixed or alluvial situations with modification to the above parameters. There is however, a large central part of the above diagram, which is undifferentiated or unassigned, into which any soils which are a mixture of end members (for whatever reason) will fall. One measure of the sharpness of the soil extraction technique, and the efficacy of the data synthesis procedure is the number of “undifferentiated”

soils which arise from test cases in various regolith and geographic situations. Another test of the usefulness and robustness of the system is the degree of coherency of the different lithological domains produced. Two examples will be briefly examined.

### The Mount SE, Widgiemooltha, Western Australia

This area, 80km SW of Kalgoorlie in the Eastern Goldfields of Western Australia was mapped at the 1:40,000 scale prior to systematic soil sampling on a 100 x 25m sampling grid. The area contains some outcrop, but also includes large areas of colluvium. The geology map (at 1:40,000 scale), a portion of which is shown in Figure 11(a) indicates a single tremolite contact between high magnesian basalt and a peridotite unit trending NW-SE for this area.

The inferred geology map (Figure 11(b)) shows large coherent domains sub-parallel to the known geology; rather than just one contact (two flows) there is however a series of inferred mafic/ultramafic domains, trending NW/SE. In addition, within the main mafic unit to the north-east, there is a large area indicative of “felsic intrusives”. Subsequently, weathered rocks verifying the felsic intrusives, were located in the predicted locations. To the south there is a very significant area (with respect to Ni exploration) of fertile or contaminated ultramafic (very high Ni and high Ce). Weathered subcrop indicating the existence of channel flow ultramafic rocks were located in this area, and exploration (geophysics and drilling) is on-going.



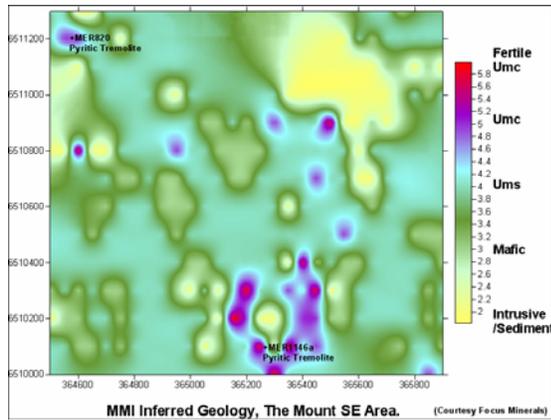
**Figure 11(a):** Geological map of The Mount SE, showing contact between a high magnesian basalt (mafic) and ultramafic units. (Courtesy Focus Minerals)

### Wongan Hills, Western Yilgarn Craton, Western Australia

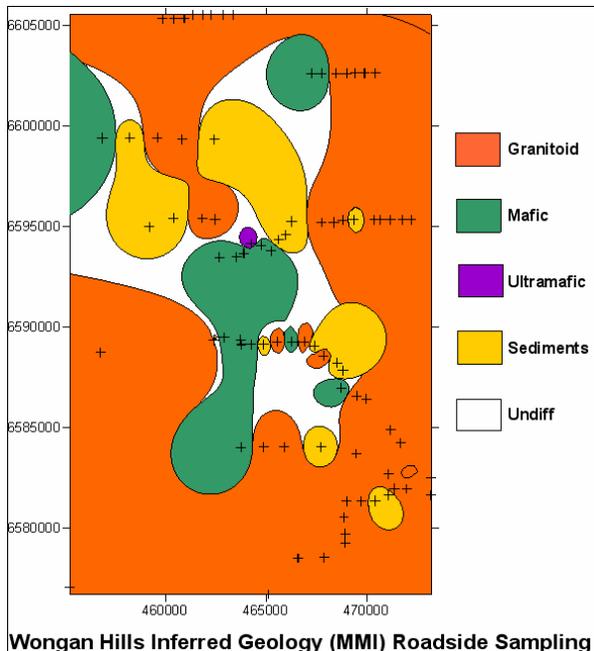
A series of roadside samples were taken in the Wongan Hills area, 120km NE of Perth, Western Australia, and known to contain a greenstone belt, in order to ascertain whether or not low-density soil sampling could detect and delineate greenstones in the wheatbelt of Western Australia. Most of the area is extensively weathered and lateritised, and much of it under cultivation for cereal crops, although outcrop is sporadically available for confirmation. Figure 12 shows the inferred

geology map obtained from a series of irregularly spaced roadside samples on several E-W traverses.

The greenstone belt has been delineated by the soil geochemistry, including a very small area of ultramafic lithology in the centre. The areas outlined as mafic, ultramafic and sediments (BIF) agree well with that shown on the 1:250,000 scale geological map sheet (Low et al, 1982). Only a relatively limited number of samples are "undifferentiated" or of mixed lithology. Both the greenstone belt and surrounding granitoid(s) plot as large coherent units. This greenstone is the subject of on-going exploration.



**Figure 11(b):** Inferred geology map of the same area, showing a series of mafic/ultramafic flows, felsic intrusives to the north east, and fertile channel flow ultramafics to the south



**Figure 12:** Inferred geology, Wongan Hills from roadside soil geochemistry.

## DISCUSSION AND CONCLUSIONS

The last decade has seen some changes to exploration geochemistry which relate more to improvements in resolution rather than radical changes in concepts and methodology. In some ways this is similar to the changes which have taken place in geophysics. Improvements in instrumentation, innovations in analysis and element suites available, and better software packages for data presentation have all contributed. Whether or not partial digestions and partial extractions are a significant improvement to conventional geochemistry (based on total digestion of the sample) is an item for legitimate and contentious debate. Many of the answers lie in the mindset of the observer – soil geochemistry for mineral exploration has for many years, at least in tropical and semi-tropical terrains, been the exclusive domain of total digestion and "assay" of samples. Some "traditionalists" find it hard to accept that there is an alternative, and possibly better method. In many cases some of the objections leveled at partial digestions and extractions have been poorly considered and selectively applied. For example, many are skeptical because there is not yet a single, accepted coherent theory for the upward migration of ions to surface. This is a factor which is fundamental to formation (and continued maintenance) of any geochemical anomaly irrespective of whether it was portrayed by a conventional or a "more esoteric" method. It is not incidentally, completely untrue – despite the fact that a number of mechanisms including electrochemical, diffusion, groundwater pumping, convection and capillary rise have been put forward (e.g. Hamilton et al, 2001, Mann et al 2005), no single mechanism has yet been shown to be capable of adequately explaining all geochemical processes in all situations. Some very important Pb isotope data and information on sampling techniques and horizons (Hamilton et al, 2001), has confirmed that ionic migration to the surface from oxidizing ore-bodies for example is a very real occurrence. Whilst a conceptual model to explain the resultant fundamental differences observed between anomalies generated by total and partial digestion/extraction has been proposed (Mann et al, 1998), research to define a cogent theory for the vertical migration of ions to form these geochemical anomalies is still on-going. The fact that empirical observations regarding the efficacy of partial digestions and extractions and implementation of the technology have preceded a fully established theory for anomaly emplacement is not in itself cause for concern. It is the nature of most major scientific advancements that empirical observations are made prior to hypothesis, experimentation, modification and theory. It is commercial reality that while some in mineral exploration see early adoption of a new technology as "an opportunity" others with a more conservative approach prefer to wait.

This is not to say that caution and skepticism are not natural or are not required. Any geochemistry, partial digestion and extraction geochemistry included, has its limits, particularly in recently transported or active alluvial or aeolian terrain. In such environments there is a conflict between accumulation of (anomalous) geochemical signal in soil from sources beneath versus removal of it by surface mechanical dispersion and dilution. In cases of extreme surface transport, anomalies are removed or replaced faster than they are formed. It has to be

said however, that high resolution techniques are allowing soil geochemistry to be used effectively further into active transported terrain. Inter-dunal sampling, for example, combined with ligand based soil extraction has provided useful soil geochemistry for exploration in desert areas of Australia. Regional and semi-regional surveys, with initial sample lines up to 2km apart, allow vast tracts of ground to be covered with good cost efficiency. With such surveys it is important that (a) samples along lines remain relatively closely spaced (e.g. 100m) and (b) follow-up and infill sampling when some initial anomalous values are encountered is systematic and thorough. Another regional exploration strategy for which high resolution geochemistry is potentially suitable is over-bank sampling. In appropriate terrain, and with careful selection of sampling sites, high resolution soil geochemistry of over-bank samples will permit large parcels of land to be prioritized for exploration. In a similar manner such samples may also be used for agricultural/environmental assessment and mapping, given the parallels between extraction of adsorbed ions and “bio-availability” and “lability”.

The additional cost of high resolution, multi-element surveys is a factor which is sometimes used by management to maintain that standard or conventional geochemical methods with a restricted number of elements are sufficient. It is hard to argue that there are not some cases where this is true – many close to surface ore-bodies have in the past been located without soil geochemistry at all. There are certainly some deposits in residual terrain which many geochemical methods, including the cheapest, are capable of revealing. In other terrain types, particularly stable exotic terrains, ionic signatures, whilst present, are subtle, and capable of resolution only with the highest resolution techniques. It has been shown in this paper that the additional elements from a multi-element survey can be used constructively to elicit additional lithological information which is relevant to mineral exploration in areas with and without cover. The current degree of sophistication in exploration (and in particular the cost of drilling) dictates that additional resolution (both spatial and amplitude) from multi-element partial extraction techniques more than outweighs relatively small front-end cost factors. Geochemistry has made progress in the past decade – much of it is yet to be embraced and implemented by the mineral exploration industry on a routine basis.

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