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Mobile Metal Ions in the A horizons of soils

#### Mobile Metal Ions in the A Horizons of Soils

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#### NON-SELECTIVE EXTRACTION

Non-selective extraction is based on the notion that by providing an extractant with a sufficiently strong ligand (for a particular metal) then a proportion of that metal will be removed from the soil. Metal will tend to be removed from those sites within the soil which become energetically unfavourable compared to the complexed state of the metal in solution, irrespective of the specific chemical or physical nature of the component of the soil to which it was formerly attached. Metals within the soil are thus classified as 'bound' or unremovable, and 'unbound' or extractable on this basis. These terms are operationally defined (by the strength of the ligand). Figure 1 depicts this in a pictorial representation of a soil particle for the case of Cu.

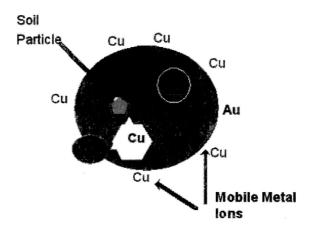


Figure 1. Bound and unbound metals in a soil.

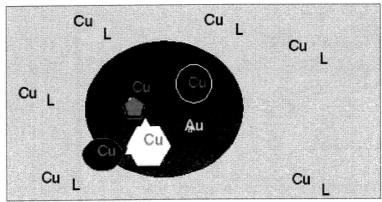
Examples of non-selective extractants with a single complexing ligand include BLEG (Bulk-Leach Extractable Gold) which uses cyanide for Au, and Deep Leach and Regoleach which use weak mineral acids for a range of metals. There are a number of problems however which can arise when a single ligand such is used as the complexing ligand for a range of metals. There are environments (e.g. acid or strongly reducing) where a strong ligand such as cyanide ion is potentially chemically compromised. Whilst it is possible to initially extract many metals (in fact a significant proportion of the periodic table) with the chloride ion e.g. from dilute HCl, the ligand strength may not be sufficient to retain all elements initially extracted in solution through the course of the analysis. This latter problem which simply occurs because chloride is not the optimum ligand for a number of metals, is referred to as readsorption. A related problem with the reproducibility of extraction and analysis can occur when a single ligand is deployed to ensure extraction and solution retention of a number of metals from a number of different samples. This can arise from competition from other metals for the available ligand.

#### MOBILE METAL ION (MMI) EXTRACTION

By providing an extractant solution with a number of optimum ligands (at least one for each metal), a number of these problems can be overcome. Thus the MMI-A extractant solution consists of a number of water-soluble organic and inorganic components, which provide ligands for the optimum dissolution of base metals Cu, Pb, Zn, and Cd. This is a weak acid.

Figure 2 shows pictorially how the ligand L in MMI-A specific for Cu, attaches and complexes with the Cu ion in solution, ensuring its solubility.

## After 24Hrs in Extractant "A"



#### Mobile Metal lons

Figure 2 Schematic model of Mobile Metal Ions being leached from a soil particle by the chemical action of a weak digestant.

Similarly, MMI-B contains a number of ligands in a weak base suitable for optimum extraction of Au, Ag, Ni, Co, and Pd from soils. Note that in each case, it is the specific intention to minimize attack on the substrate, and to release a significant, but minor proportion of the total metal, usually between 5% and 50%. This not only ensures compliance with the adsorption isotherm requirements above, but also, as we will see, ensures some very significant improvements in background and signal to noise ratio. Table 1 shows the range of MMI extractions currently available, or currently under investigation.

Table 1. Range of MMI extractions currently available, or currently under investigation.

Extractant	Target	Elements	
MMI-A	Base Metals	Cu, Pb, Zn, Cd	
MMI-B	Precious Metals	Au, Ag, Ni, Co, Pd (Pt)	
MMI-C	Base Metals (high carbonates)	Cu, Pb, Zn, Cd	
MMI-D	Kimberlites (diamonds)	Ni, Nb, Cr, Mg, Pd, Mn	
MMI-E	Majors, lithogeochem	Ti, Fe, Si, Mg, Ca, Th, Zr, Sc	
MMI-F	Pathfinders	As, Sb, Mo, W	
MMI-G	Granophiles (Pegmatophiles)	U, Pb, Th, Sn, Li, Ta	

It is implicit in the MMI approach, that the number of elements in the extraction suite is limited, in order to optimise the extraction efficiency for each metal contained in the suite. As shown in the above table, the extractants are therefore designed for complexing a particular (limited) suite of elements, and are designed for a particular geological target or targets.

### STANDARD REFERENCE MATERIALS, REPRODUCIBILITY

In any geochemical survey, it is important to maintain a check sample program independent from that undertaken by the laboratory. One standard reference material and one duplicate sample should be inserted within each sequence of 50 samples to monitor precision and accuracy. QC samples should be inserted as part of the numbering sequence but not essential. It is essential to know to what degree of precision, the duplicates and standards should replicate.

In any analysis scheme, and particularly for partial digestion methods such as MMI, there are a number of possible sources of error, each of which contribute to the error or non-reproducibility. Error can arise at the extraction stage as well as the instrument reading stage. In a comprehensive survey of the sources of error in the MMI technique, and the errors introduced at a number of stages, were investigated. A summary of the outcomes is shown in Table 2.

Table 2. MMI-A and B Analysis - Reproducibility Summary.

Category	Results (C of V or R squared)	Conclusions				
Spiked solutions. 1000ppb	Cu 4.2% Pb 3.3%	ICP-MS is reproducible				
solutions of Cu, Pb, Zn and Ni.	Zn 5.2% Ni 5.6%	ICP-MS is accurate				
100ppb solutions of Au, Ag, Cd, Co	Cd 3.0% Au 3.2%	MMI-A is suitable analyte				
and Pd, in MMI-A & MMI-B.	Ag 4.1% Co 6.7%	MMI-B is suitable analyte				
·	Pd 5.2%					
2. Splits of a single homogenized	Cu 10.6% Pb 10.6%	Average C of V 7.8%				
bulk sample. Same ICP, same	Zn 2.1% Ni 7.4%	Zn the best				
digest, same day. (Wamtech data	Cd 2.3% Au 5.9%	Co the worst				
base, n=6.)	Ag 4.5% Co 23.0%	Reflects intra-batch ICP variation.				
	Pd 4.2%					
3. Splits of a single homogenized	Cu 15.5% Pb 19.4%	Average C of V 14.2%				
bulk sample (HBS). Same ICP &	Zn 15.3% Ni 10.0%	Au the best				
lab over a period of time.	Cd 21.7% Au 5.7%	Co the worst				
(Wamtech data base, n=11-16.)	Ag 6.9% Co 24.6%	Reflects lab, digest and time				
	Pd 8.5%	variations.				
4. Splits from a non-homogenized	Cu 18% Cu 21%	Average C of V's 14.8%, 21%				
sample, same digests, same labs	Pb 22% Pb 25%	Laboratory difference				
for MMI. (Replicate analysis set	Zn 8% Zn 20%	Similar to HBS.				
of 12 samples sent to 2 labs.)	Cd 11 % Cd 16%	Little intra-sample variation.				
	0 15.00/	Homogenize standards.				
5. Same as above for	Cu 15.3%	Average C of V 14.3%.				
conventional analysis comparison.	Pb 13.6%	Basis for comparison				
	Zn 13.3%					
	Cd 14.9%	c.f. Eggo, R <sup>2</sup> =0.97 for ICPMS				
6. Replicate samples, different	Regression Analysis (R <sup>2</sup> )	Good linear discrimination over a				
sites, same lab, same digest.	Au = 0.998 Ag = 0.999 Ni = 0.982 Co = 0.986	wide range.				
		wide range.				
D. C. J. Hillard at	Pd = 0.988  7. Replicate samples, different Regression Analysis (R <sup>2</sup> ) c.f. Eggo, R <sup>2</sup> =0.97 for ICPMS					
7. Replicate samples, different	Au = 0.993 Ag = 0.998	Use same laboratory whenever				
sites, different labs, different	Ni = 0.957 Co = 0.865	possible.				
digests.	Pd = 0.901	possible.				
2 Different complex from 1 Em	Anomalous site Background	Small site sampling variation.				
Different samples from 1-5m radius of anomalous (A) and	Au Mean 3.3ppb 0.4ppb	Percentage increases as values				
background (B) site. (Wamtech MG	Au C of V 13.6% 24.9%	approach L.D.L. of instrument.				
	Ag Mean 13.6ppb 1.8ppb	approach Elbibio				
data, n=26.)	Ag C of V 15% 23.9%					
Different samples from same	Au=3.7ppb(15.7%)	Anomalies and backgrounds				
sites after an elapsed (rainfall)	Ag=10.2ppb(17.2%)	maintained across significant				
period.	X-Y scatter plots for Cu, Cd, Ni and	rainfall events.				
periou.	Au from Nepean East					
10. Different samples composited.	Average variation from arithmetic	Compositing samples is an option.				
Compare analysis with arithmetic	mean:	, , , , , , , , , , , , , , , , , , , ,				
mean. (Wamtech data, n=6)	Ni 11.2% Au 8.5%					
mount (vanitoon data, n=0)	Ag 19.8% Co 9.8%					

Whilst the coefficients of variation in general increase from the first (top) category to lower in the table as the number of analytical steps increases, the absolute values are very comparable to those involved in any geochemical analysis. It is of interest that not all elements have identical C of Vs; in general Co has higher values than (say) Au, for which the procedures and the ICP-MS are very suitable. All regression curves (categories 6 and 7) were very linear, proving the technique is suitable over a wide analytical range.

In summary the conclusions of this study were:

- (1) that ICP-MS is a very suitable instrument for analysis of MMI extracts;
- (2) that MMI extracts A and B are suitable analytes;
- (3) coefficients of variation are comparable with those of conventional (total) digestion on bulk homogenized samples;
- (4) samples for a survey should be submitted as a single batch if possible;
- (5) the same laboratory should be used wherever possible;
- (6) lateral variation of mobile elements at a sample site is very small;
- (7) vertical differentiation of both mobile and total metal at a sample site is of greater concern;
- (8) for this reason samples should be 500 g or less, and selected from 5-15 cm below surface;
- (9) rainfall has a minimal effect on mobile metal ion values; and
- (10) compositing of samples is a viable option.

#### MOBILE ION SIGNATURES IN THE A HORIZON

Analysis of vertical profiles conducted early in research programs (for example as shown in Figure 3), indicated that a significant proportion of the mobile form of each metal is located in the upper (A horizon) part of the soil. In some cases, as in that shown in Figure 3, the A horizon is exotic.

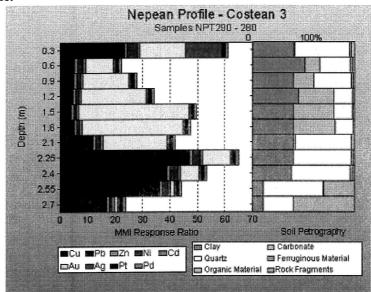


Figure 3. MMI analysis of various metals in a costean at Nepean Ni mine.

A large number of laboratory experiments were then carried out to elucidate the mechanism of this transfer of metal within the solum (the A & B soil horizons). Included in these were experiments which showed that capillary rise and evaporation are extremely important in the formation and preservation of the mobile ion signals in the A horizon. The results of one of these experiments are shown in Figure 4.

In this particular experiment, a self-watering flower pot containing barren silica sand has had a pregnant solution containing 1ppm of Cu, Pb and Cd placed in the well beneath the pot. Within one week measureable concentrations of Cu and Cd (measured in an MMI-A extract) are evident in the near-surface, some 15cm above the lower well. The concentration for Pb (less mobile) increases above background several days later. It is evident that processes involving mobile metal ions are rapid, and that processes in the solum are dynamic.

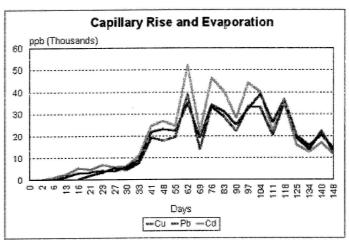


Figure 4. Accumulation of Cu, Pb, and Cd in the surface layer of coarse silica sand.

Sampling for MMI is normally recommended at a depth of 5-15cm, to ensure that it is the A horizon which is sampled, and to minimise contamination from sticks, leaves, etc. The soil is roughly sieved, e.g. to 3-4mm.

#### **CARBONATES**

The strong dependence of solubilities of base metals on pH is well known. Soils which contain appreciable concentrations of carbonate require special attention because of this. Whilst leachants such as MMI-B which are basic are relatively unaffected, mild acid leachants such as MMI-A have to be monitored carefully in that there is likely to be a soil-carbonate concentration beyond which they may not be expected to operate. Firstly however, and as illustrated in Figure 5, there is a significant pH difference between the natural pH of a soil (or synthetic soil) and the pH during a 1:1 extraction with MMI A.

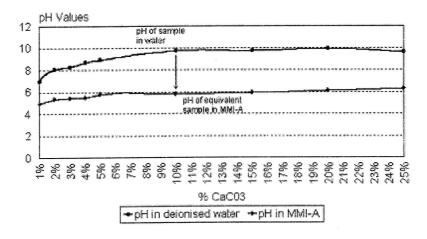


Figure 5. Comparison of pH of synthetic carbonate samples in water and in MMI-A.

As shown above, natural or synthetic soil samples are almost 3 pH units more alkaline than the equivalent sample in an MMI-A solution. Given the shape of the base-metals versus pH solubility curve, it can immediately be stated that base metals will be less soluble (more immobile) in a soil in the natural environment (e.g. after a rainfall event) than during a digestion procedure on the same soil. We do however need to carefully examine the behaviour of any given extractant, to establish its "working range", from both a pH and carbonate perspective, and to assure there is little or no dependence of extracted metal on pH over this working range. Table 3 shows the concentrations of Cu, Pb, Zn, and Cd extracted by MMI-A solution from two samples after various amounts of NaOH are added to provide a (limited) range of pH values.

Table 3. Concentrations of Cu, Pb, Zn and Cd extracted by MMI-A from two samples at different pH values, obtained by various additions of sodium hydroxide.

Sample	pН	Cu	Pb	Zn(ppm)	Cd
SA226	2.47	1250	1770	45.2	106
SA226	2.85	771	1150	44.7	98
SA226	3.58	1000	1080	57.7	98
SA226	4.25	1090	1310	60	92
SR70	2.73	45	15	0.947	28
SR70	3.33	51	12	0.956	25
SR70	4.12	69	16	0.984	23
SR70	4.6	70	16	0.895	23

Over this pH range, there is very little dependence of the amount of metal extracted on pH. Accordingly this weakly buffered extractant is suitable for extraction of base metals in soils with small amounts of carbonate.

The limit to which any extractant (whether it be strong acid, a buffered solution, or weak acid) can tolerate carbonate is governed by the simple neutralisation reaction, which indicates that for every 1g of calcium carbonate in the sample, 20 millimoles of acid is consumed. Experiments with MMI-A demonstrate that solubilities of Cu, Zn and Cd up to 10 ppm can be maintained for pH to 6.5 (soil carbonate up to approximately 25%  $CaCO_3$ ). For Pb, concentrations are comparable with those in water, and above a resulting solution pH = 5.5 (10%  $CaCO_3$ ) Pb solubility is very restricted, presumably due to the formation of lead hydroxy-carbonate.

For samples with higher carbonate content (resulting pH) than this, MMI-A is not recommended. A separate leachant, MMI-C, and a different laboratory protocol are required. In practice, only a relatively small number of soil samples require special treatment (i.e. have high carbonate contents).

## METAL AVAILABILITY IN (CARBONATED) AGRICULTURAL SOILS

Partial digests have been used in agriculture for over 25 years in order to obtain a measure of the availability of metals to plants. In many cases a definite linear correlation is observed between the available metal concentration, and the natural pH of the soil sample. Two examples (Lindsay et. al., 1972) are shown in Figure 6.

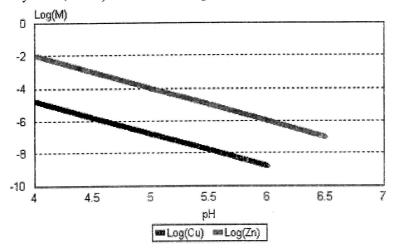


Figure 6. Relationship between Metal Activity and pH (Agricultural Soils, after Lindsay *et. al.*, 1972).

Although Zn is shown to be more available at a given pH than Cu, both show a linear dependence on pH, and therefore implicitly on soil pore water carbonate ion concentration. Similar correlation has been observed in some mineral exploration surveys in carbonate terrain with MMI-A. These have been within a pH range in which the efficacy of the MMI-A extractant is not compromised by the carbonate content nor pH (i.e. below CaCO<sub>3</sub> contents of 15%). Given the previously demonstrated relative independence of the extracted concentrations of base metals and pH of the MMI-A extractant, the effect is almost certainly due as in the agricultural examples, to a natural dependence of base metal mobility on soil pH and carbonate content i.e. base metals are in general less mobile in carbonate-containing environments than those without.

In a study of various extractants on English soils (Tills & Alloway, 1983), which included some chalk soils, it was found that EDTA, a weak acid extractant with strong ligand complexes with base metals, produced the best correlation with plant uptake of Cu. In this study, the correlation was between Cu content in digested plant material, and soil extractable Cu during growth. The study included dilute nitric and hydrochloric acids as weak extractants which gave poorer correlation than EDTA. It is also commonly observed in such studies that correlation between total metal content and availability (and uptake) is not good, i.e. that some soils with high base metal concentration, contain metal in a 'bound' form which is unavailable to plants. There are conceptual parallels between the "available metals" of agricultural science, and the "mobile metals" referred to here.

# CASE HISTORIES 1. SAN JORGE, ARGENTINA

This study has been supported by: Grupo Minero Aconcagua S.A., a wholly owned subsidiary of Northern Orion Explorations Ltd, MMI Technology, the developers of Mobile Metal Ion technology, and XRAL Laboratories, a laboratory licensed to undertake MMI analyses. W.C. Williams, Project Geologist at San Jorge, and J. Madrid implemented and completed the sampling programme.

The San Jorge Cu-Au project (see Figure 7) is located approximately 100 km northwest of the city of Mendoza along Route 39 some 40 km north of the village of Uspallata. It is in the Uspallata Valley situated along the eastern flank of the Cordillera Frontal. Elevation is between 2600 and 2685 masl. A desert climate predominates and low-lying vegetation covers the area. No surface water passes through the project area.



Figure 7. Photo overlooking the sampling area at San Jorge in the foreground with mountains in the background.

The San Jorge Cu-Au deposit is at the southern end of a north-south trend of various hydrothermal deposits that outcrop for over 300 km in the Uspallata Valley and its environs. The country rocks are Devonian phyllites, Carboniferous clastics, and Permo-Triassic extrusives that host felsic Permian and Tertiary porphyritic stocks. Unconsolidated gravels, derived from the Cordillera Frontal to the west and Precordillera to the east, filled the valley after Andean uplift in the Tertiary.

San Jorge is a porphyry copper deposit (PCD). It is hosted by the Carboniferous clastics, a felsic porphyry intrusive, dacitic dikes, and a tourmaline breccia. The former is host to higher-grades of hypogene mineralization. The tourmaline breccia and dacite dikes host a volumetrically small portion of the deposit.

The principal structures strike NS to NNE; NW and ENE faults are secondary structures. Even though displacements are not significant, the faults and their related structures were important conduits for meteoric waters that promoted leaching of sulfides, deposition of copper oxides, and the formation of an enriched blanket.

The San Jorge PCD is characterized by potassic, phyllic, and propylitic alteration that is distributed unevenly throughout the deposit. Biotite and tourmaline are the earliest alteration events followed by potassium feldspar alteration as haloes around quartz-sulphide veinlets as well as a replacement of plagioclase; two centres of potassic alteration have been identified. Silicification with subsidiary sericite, i.e., phyllic alteration, affects all rock types. Hairline calcite veinlets, with or without clay or quartz, crosscut all other alteration types and represent the propylitic alteration.

The mineralization trends northeast-southwest. Copper occurs in malachite, chrysocolla, pitch limonite, chalcocite, covellite, digenite, and chalcopyrite; brochantite, azurite, tenorite, native copper, cuprite, and bornite are minor. Mineralization has been divided into five (5) zones: 1) gravels, 2) leached, 3) oxide, 4) enriched, and 5) primary. The oxide body is best developed along the western contact of the granite porphyry with the sedimentary sequence and in the southwest sector of the deposit under gravel cover. Secondary sulphide mineralization occurs as sooty chalcocite in areas of intense faulting and repetitive water recharge, e.g., southwest sector, as well as chalcocite, covellite, and/or digenite rimming chalcopyrite in 'transitional zones'. Three (3) high-grade zones (>0.5%) of primary mineralization are hosted by the sedimentary sequence. Copper grades can exceed 1.0%, and intervals that contain up to 0.5% copper have been encountered to depths as much as 495 m. Native gold occurs in all ore zones averaging approximately 0.2 ppm throughout the deposit. Silver is sympathetic to copper, at a ratio of 1 ppm Ag per 1250 ppm Cu.

Three east-west, and two north-south lines for a total of 95 samples were sampled 10-30 cm below surface. Sample material was typically unconsolidated sands and gravels with cobbles at surface. Samples were extracted and analysed by XRAL Canada. Elements Cu, Pb, Zn, and Cd were analysed following the MMI-A extraction and elements Au, Ag, Ni, Pd, and Co following MMI-B extraction. The MMI results for section 8650E, which traverses the known mineralization, including the southwest sector of the deposit where high-grade copper is encountered in the oxide, enriched, and primary ore zones, are shown in Figures 6 & 7. Figure 10 is a cross section along line 8650E, showing geology and sub-surface mineralization.

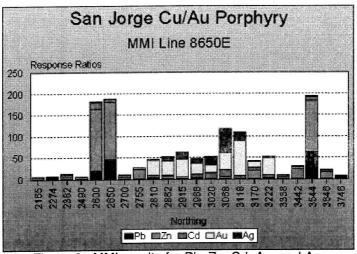


Figure 8. MMI results for Pb, Zn, Cd, Au, and Ag.

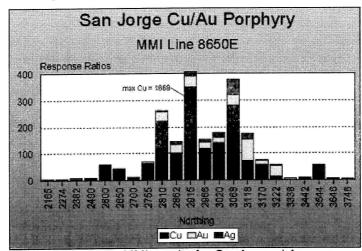


Figure 9. MMI results for Cu, Au, and Ag.

There are a number of interesting features when compared with the MMI results across this line. Firstly, there is a zonation pattern across the deposit, with outlying anomalies of Zn and Cd giving way to anomalous Cu, Au, and Ag over the primary and enriched zones of the deposit. Secondly, whilst Cu is present in considerable concentrations and reports very strongly in the MMI geochemistry, Au and Ag also report with very strong MMI response ratios over the mineralization, considering the tenor of the Au mineralization (average 0.2 ppm). Thirdly, given the varying depth of the gravel cover (and the existence of carbonate hardpan at 1.5-2m), the MMI geochemistry has provided a sharp and accurate surface outline of the sub-surface mineralization, with response ratios for Cu of over 100 times background, and Au and Ag response ratios of over 50 times background.

The study also identified elevated MMI geochemical responses coincident with IP geophysical anomalies as well as offsetting a drillhole with good Cu intercepts. Both areas have approximately 100 metres of gravel cover. Further work is required to assess the relevance of these data.

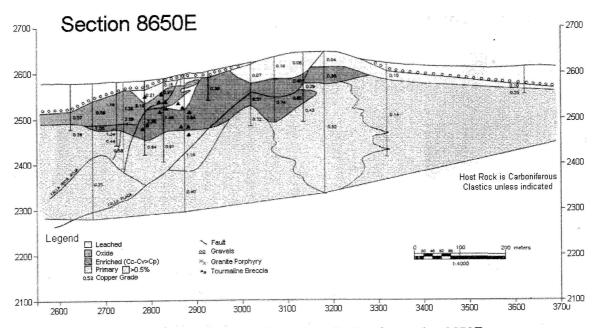


Figure 10. Geology and sub-surface mineralization for section 8650E.

The implications for exploration are:

- 1) The multi-element suite for MMI provides a useful and elegant surface indication of the zonation within porphyry systems.
- 2) The MMI technique can provide useful surface geochemistry through veneers of gravel in Andean type environments.
- 3) The MMI technique can provide surface geochemical indications that are sufficiently sharp and accurate to enable accurate placement of drill-holes in these environments.
- 4) As other MMI studies have shown, it is important to maintain a consistent sampling depth below surface to avoid variation caused by vertical metal partitioning within soil profiles.

Grupo Minero Aconcagua, S.A., a wholly owned subsidiary of Northern Orion Explorations Ltd provided the San Jorge site for the orientation survey. Dr W.C. Williams, and J. Madrid implemented and completed the sampling programme as well as reviewed the text for accuracy. The hospitality and assistance given by Northern Orion staff were greatly appreciated.

#### 2. SAN NICOLAS

The San Nicolas Project is located 65 kilometres of the city of Zacatecas, Mexico. The Project is a 55/45% joint venture between Teck Corporation and Western Copper Holdings Limited. The partners commenced exploration in mid-1996 within an area typified by gently rolling topography at an altitude of 2100 meters. Initial work focused on previously known copper mineralisation at the El Salvador prospect. Expansion of exploration activities identified the San Nicolas area as prospective based on limited exposures of favourable altered volcanics.

An initial drill target was identified by a follow-up geophysical survey that defined a strong induced polarisation (IP) chargeability anomaly measuring 500x500meters. The first hole into the anomaly was drilled in November 1997 intersected 175 meters of massive sulphide mineralisation starting at a depth of 205meters below the surface.

To date in excess of 50 drill holes have intersected the massive sulphide mineralisation.

The San Nicolas "VMS" deposit contains a zinc rich zone at the top and a copper rich zone at the base. The zinc zone contains 34 million tonnes of 4.28% Zn and 0.76% Cu; while the Cu zone has 38 million tonnes grading 1.89%Cu. A preliminary mineable open pit reserve of 72 million tonnes grading 1.35-%Cu, 2.27%Zn, 0.53g/tAu and 30g/tAg has been defined. (Acknowledgements: Teck Corporation - <a href="www.teck.com/ops/adv/adv\_san.html">www.teck.com/ops/adv/adv\_san.html</a> and western Copper Holdings Ltd - <a href="www.westerncopper.com/sannic-4s.html">www.westerncopper.com/sannic-4s.html</a>)

A preliminary orientation survey was undertaken at San Nicolas to test the MMI geochemical technique. The site has an arid environment with highly carbonated soils above economic base metal mineralisation, covered by a significant thickness of barren overburden. The typical section above the mineralisation for the MMI orientation line was: Surface gravels – 10 to 20 meters containing a caliche horizon, Tertiary volcanoclastics – 60-80 meters, hanging wall mafic volcanic flows and sediments – 100-160 meters, depth to mineralisation – 180 to 240 meters. Surface samples were collected at 30m intervals along the line.

The dominant MMI element was Pb with subsidiary Zn, Cd and Cu responses. Lead has a peak response of 20 times background as shown in Figure 11. There were no conventional geochemical responses reflecting the known base metal mineralisation.

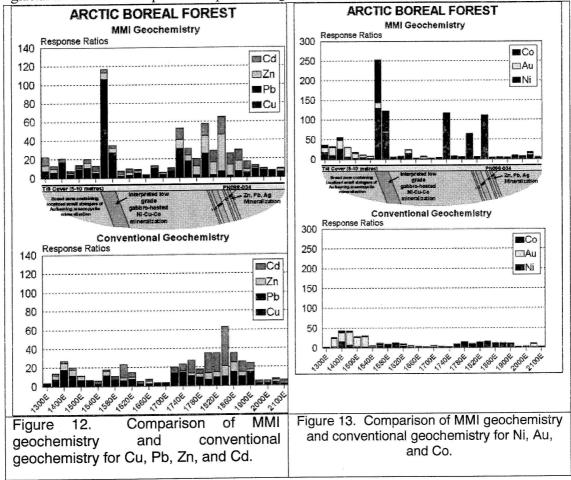
One anomalous Au zone was defined immediately adjacent to the known mineralisation, an association typically seen in MMI data over VMS deposits. On the opposite side of the deposit, some 200 meters, the last sample (11662) returned a 25 times background Au response.

### San Nicolas MMI Geochemistry Response Ratio 25 20 15 10 Sample No waa Cu waa Pb maaZn Gravels 1-8m thick with caliche. Tertiary Volcanics Mineralized Zon 150-200m belov Package of mafic volcanics surface. sediments, tuffs. 72m tonne @1.35% Cử 2.27% Zn. Total Digestion Response Ratios 20 15 10 5 Sample No. BECU SEPB EMZn

Figure 11. MMI and Conventional Geochemistry, San Nicolas.

#### 3. ARCTIC BOREAL FOREST, EUROPE

The MMI data, and conventional data from an acid digest procedure, from soils taken from glacial till cover in Europe are compared in Figures 12 and 13.



Again, the same response ratio scales have been used for the comparison. In this project, the traverse has been placed over three zones of potential interest, (a) stringer-related gold-arsenopyrite mineralisation, (b) gabbro-hosted Ni-Cu-Co mineralisation, and (c) sub-economic base metals mineralisation. For elements such as Au and surprisingly Cd, the MMI and conventional geochemistry signal to noise ratios are similar or slightly superior for conventional geochemistry over the stringer Au and base metals zones. For all other elements, response ratio contrast is higher for MMI geochemistry over zones containing mineralisation. Both samples, in this case were taken from the A horizon. In this type of environment, the B horizon is difficult to locate, and the C horizon is below the 5-10 m of glacial till.

## COMPARISON OF MMI AND CONVENTIONAL GEOCHEMISTRY

Comparing the outcomes of partial digestion geochemistry, and conventional (total digestion) geochemistry, achieves two things. As well as providing useful information for the explorationist, it also provides a very good insight into the processes that give rise to the formation of a geochemical anomaly. As noted in the previous chapter, two aspects or attributes of the geochemistry are of particular relevance – the sharpness of the peak over mineralization, and the strength or peak to noise ratio of the anomaly. Together these two features describe the resolution of the particular geochemical technique.

In relation to resolution, comparison of MMI versus conventional or total digestion appears to produce a number of outcomes, dependent on the geological setting, and the elements involved:

- 1. MMI and conventional geochemistry sometimes show similar anomaly patterns. These involve elements with limited mobility such as Au and Pb. In the case of Au there are additional false anomalies with total digestion (these may constitute a separate category).
- 2. Commonly MMI exhibits higher resolution than conventional geochemistry, both spatially, and with respect to the amplitude of the anomaly relative to background.
- 3. Sometimes there is recognizable contrast with MMI, but insignificant contrast by conventional techniques. This case is often observed with the more mobile elements such as Zn, Ni, and Cd.
- 4. Situations where both types of geochemistry fail to register the presence of underlying mineralization do occur. Such cases are restricted to either deep burial, or zones of very active transport, e.g. aeolian dunes or active alluvial channels.
- 5. Examples where conventional geochemistry provides greater contrast than does MMI. Appear to occur very infrequently. They are limited to those situations where fresh mineralization is at/or very near the surface.

The approximate percentage distribution of these outcome types is shown in Figure 14.

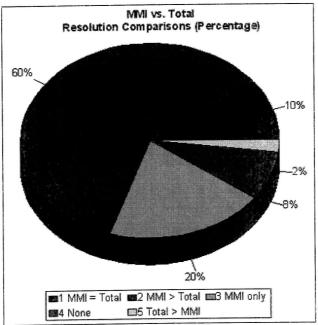
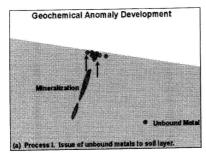
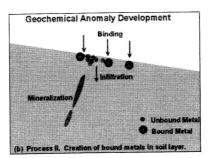


Figure 14. Approximate distribution of resolution comparisons: 1 – MMI = Total, 2 – MMI > Total,3 – MMI only, 4 – None, 5 – Total > MMI.

## A SIMPLE GEOCHEMICAL MODEL FOR THE SOLUM

A simple three step geochemical model has been proposed to explain these features. It proposes that a dynamic balance exists in the solum between metals in the unbound and bound forms. The model is shown pictorially in Figures 15(a), (b), and (c).





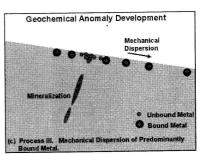


Figure 15(a-c) Geochemical anomaly development stages.

Three processes are considered to be important:

<u>Process 1</u>. Metal input to the A and B horizons as depicted in Figure 15(a) is considered to be ionic in form, and derived from the oxidation of underlying sources and vertical migration. It is essentially a point source input, directly related to the source area (or areas) beneath. These metals constitute the unbound metals of the solum.

<u>Process 2</u>. Through the actions of principally rainfall, these unbound metals are not only subject to downward infiltration, but upward vertical migration (capillary rise and evaporation), and are also subject to being converted to the bound form by pedogenic processes. These pedogenic processes probably take place over a time period that is both long, relative to the rate of normal chemical reaction, but short relative to geological time, i.e. years to thousands of years.

<u>Process 3</u>. Both unbound and bound forms of metal are subject to the agents of lateral migration, such as mechanical creep, sheetwash and aeolian processes. These are essentially planar phenomena, i.e. they occur at all points on the surface.

However, the unbound form is constantly being converted to a bound form at any point on the surface or within the profile. It is only replenished close to the point source. Thus, the proportion of unbound metal decreases (and concomitantly the proportion of bound metal increases) away from the point of issue, i.e the anomaly zone. Background for unbound metals is reduced to very low levels by the conversion to a bound form. The spread of bound metal, and including background values for bound metal is greater than for unbound form. Both the sharpness, and the greater amplitude of the anomaly contrast for a partial digestion method is due to the fact that an intermediate species (i.e. one with a definitive lifetime) is being utilized.

## IMPLICATIONS FOR EXPLORATION

There are several important questions that need to be asked by the explorationist. When should a technique such as MMI, be utilised in favour of a conventional (total) digestion technique? Secondly, what can the application of a high-resolution soil geochemistry technique such as MMI do for my exploration programme? Is a technique such as MMI likely to not detect a geochemical anomaly observable by conventional methods?

The first question is best answered by referring back to the comparative case histories. The MMI technique was found to give superior resolution for most metals including Au, when the degree of weathering was great and/or surficial cover was a factor. The discrimination of partial techniques such as MMI against false anomalies from physically transported (nugget) Au has been documented on several continents. For elements such as Zn, Ni, and Cd, which are particularly mobile, the response ratio differences were appreciable. Thus, in tropical weathering terrain, or colluvial environments or those with exotic cover, the additional signal to noise ratio of the partial technique is likely to prove beneficial. For Pb in most terrain this

is less likely to be so –due to its immobility. In this respect the San Nicolas case history is interesting, in that the partial digestion for Pb with MMI-A provided significantly better resolution over the deposit than conventional geochemistry.

Where mineralisation is strong, and close to surface, any geochemical method is capable of resolving anomalous zones, and there is less difference in resolution between partial and total techniques. For exploration in residual terrain, with very little weathering, choice of a total digestion technique is justified on cost grounds, providing that, in the case of Au, it is known there is no lateral displacement (false anomalies from bound metal) problems using (say) fire assay. The penalty for incorrect interpretation of the latter can be serious – as serious as non-detection of a viable ore-body or drilling a false anomaly.

In zoned metal systems, resolution of the metal sequence (as shown in the San Jorge example) will allow the geochemical survey to be more intelligently integrated with the geological programme prior to actual discovery. In a similar manner, it is useful to know during Ni exploration which part of the system is being explored, even when it is under surficial cover. Only a precise multi-element technique can do this. From the experimental evidence, case histories so far carried out, and computer modelling it appears unlikely that a technique such as MMI will fail to register a signature for a sub-surface source which has a conventional geochemical anomaly. In short, the worst case scenario for a technique such as MMI is anomaly resolution similar to that from conventional analysis.

In relation to the benefits that might accrue from the application of a high-resolution technique, such as MMI, there are two ways in which the increased resolution can be of value. Firstly, the increased magnitude of the signal to noise ratio can be of benefit in terrain types where conventional geochemistry has resolution problems. Examples include colluvium, and areas with shallow depths of exotic cover, e.g. the Atacama gravels, glacial till, aeolian sands. It also appears likely that A horizon geochemistry, such as MMI, might be appropriate in heavily-leached temperate soils, in which conventional B and C horizon anomalies do not readily accumulate. The ease and cost of sampling the A horizon is also a benefit.

Secondly, the superior spatial resolution can be of potentially great benefit. It is manifest in a number of ways. For example, in a zoned geochemical system, the zoning is only recognisable in surface soil surveys if the geochemical method is spatially precise. The San Jorge example relies very much on the sharpness of the MMI geochemistry for each element in order to display the zoning patterns. Geochemical 'structure', for example the concentration of Au along contacts, and opposing shear systems can only be portrayed if the chemical extraction is 'sharp'. For Ni, delineation of channel-flow facies rock boundaries is only of benefit if it is also spatially precise. Confirming or supporting evidence from an accompanying element (e.g. Cd for Zn and Ag for Au) is only useful if there is good spatial coincidence. Most importantly, the additional spatial resolution can be best utilised in the accurate placement of first-round drilling. In many cases better placement of the drill can obviate reconnaissance drilling, trenching or expensive costeaning exercises.

Finally we need to examine the role of the geochemist, in interpreting "higher resolution" geochemistry. There may be a tendency for some to think that there is less need for expert interpretation due to higher resolution, or to approach the interpretation without due regard to all the possible contributing factors. Integration of landform and soil type into each geochemical survey is an important part of interpretation. Geochemistry, in particular soil geochemistry is the response to any one or a number of possible contributing sources e.g. lithology, regolith, mineralisation, anthropogenic. Defining an anomaly (by definition a relative term) requires the intervention of a geoscientist. Anomalies are not defined *per se* by the geochemical analytical results, although the ease of definition may be assisted or otherwise by the resolution available. Selection of MMI anomalies likely to be related to mineralisation sources requires the same dedication, understanding and skills as the equivalent exercise with conventional geochemistry. The successful mineral exploration

geochemist of the future will be one who chooses and uses 'higher resolution geochemistry" with due regard to these facts.

#### SUGGESTED FURTHER READING

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