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Executive Summary

Partial extractions have regained popularity as mineral exploration tools in the 1990's mainly because of the emergence of empirical data which suggests that such extractions (e.g.) are capable of detecting mineralization through transported overburden and bedrock cover where conventional extractions (e.g. aqua regia) fail to do so. In many cases, element anomalies are spatially associated with buried mineralization, but more often than not, these are isolated single-point anomalies. In traditional geochemical exploration, sample intervals are adopted to give rise to <u>two or more</u> consecutive anomalous responses over mineralization.

An investigation into the variability associated with the use of partial extractions indicates that erratic anomaly patterns, which consist of isolated single-point responses, are related mainly to high sample site variability that reflects an irregular distribution of source minerals over short intervals. In some cases, there is also considerable within sample variability for particular elements or, in other words, an extreme nugget effect. This variability can be reduced to obtain more uniform and representative anomaly patterns by composite sampling. In addition to mineralogical variations within sample sites and samples, other sources of variability include sample processing and the analysis itself. More care must be devoted to sample processing and the analysis particularly when using weak extractions that leach less that 5% of the total element concentration from soils and sediments.

(1.0) Introduction

Partial extraction analyses (e.g. enzyme leach) are thought to be superior to conventional analytical procedures (e.g. aqua regia) for detecting mineralization under transported overburden (Clark et al., 1990). Their ability to detect mineralization under such overburden relies on assumptions that (1) sulphide mineralization can oxidize under transported overburden to release elements to groundwater, and (2) elements can migrate to surface in aqueous or gaseous media to become fixed in and on organic and inorganic substrates. Partial extraction techniques selectively dissolve elements held in specific forms in soils, and the spatial distribution of these elements should reflect buried mineralization. Elements held in more resistant substrates unrelated to mineralization are not extracted, and this lowers background noise considerably such that anomalies spatially related to mineralization can be identified.

This study focused on determining whether partial extractions are applicable to mineral exploration by testing extractions of variable strength over (1) copper mineralization

covered by 100 to 150 m of Upper Miocene alluvial gravels in Chile, and (2) various types of base metal mineralization covered by 1 to 40 m of Quaternary glacial drift (e.g. till) in Canada (Appendix 1). Seven orientation surveys were carried out to determine which sample media, extractions, and elements reflect buried mineralization on a consistent basis, and to establish that anomalies spatially associated with mineralization are genuine, and not simply artifacts of flawed analysis or sample processing, changing terrain conditions, or anthropogenic activity.

The main conclusion of the study is that strong and intermediate strength extractions (i.e. 30 to 100% of total element concentration extracted) outperform weak extractions (i.e. <5% of total element concentration extracted) in shallow (<5 m) transported overburden, and the opposite is true for deep (>5 m) transported overburden. Throughout the study the following anomaly patterns were identified:

(1) Isolated <u>multi-point</u> anomalies on a uniform background. This pattern is apparent in both shallow and deep transported overburden where multi-point, apical anomalies are evident over or adjacent mineralization (Figs. 1 and 2a).

(2) Isolated <u>single-point</u> anomalies on a uniform background. This pattern is more typical of deep transported overburden where single-point anomalies on a uniform background occur over or adjacent to mineralization (Fig. 2b). Type 2 anomalies prevail in this study, and they also predominate in partial extraction case studies carried out by other workers (Appendix 1).
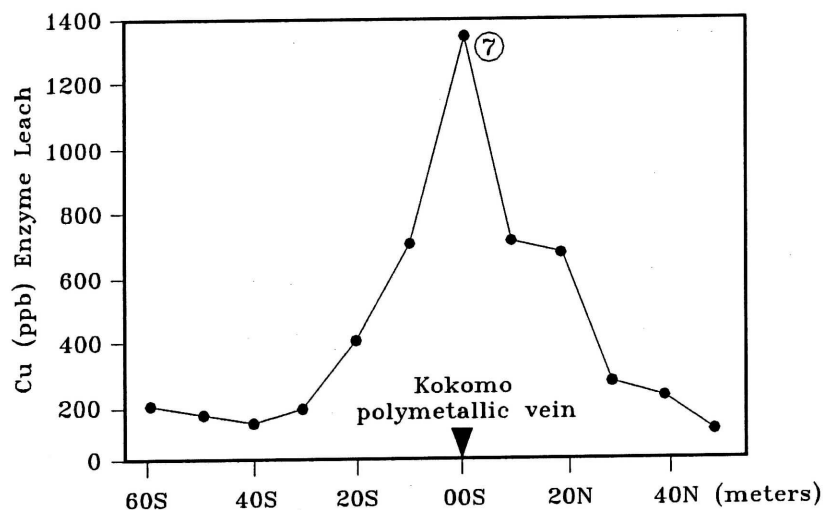

Figure 1. Distribution of enzyme extractable Cu over the colluvium-covered Kokomo polymetallic vein at Russel Gulch, Colorado (Smith et al., 1993). This Type 1 anomaly consists of anomalous Cu in consecutive samples over mineralization. The contrast is given in the circle beside the anomaly.

More statistical confidence can be placed in Type 1 anomalies, which consist of anomalous responses in consecutive samples, and these would therefore be followed up immediately (Rose

et al., 1979). Less confidence is placed in Type 2 anomalies because they consist of single points that may not be reproducible, and they could therefore be dismissed without further investigation. Type 2 patterns should not be rejected prior to understanding the underlying variability, because there could be more to these patterns than meets the eye. This part of the workshop is devoted to understanding the sources of variability associated with the Type 2 anomaly patterns. Before these anomaly patterns can be attributed to buried mineralization or other phenomena, it is necessary to confirm that the anomalies are indeed genuine, and not simply an artefact of the analysis and/or poor sample representivity. In other words, it first needs to be confirmed that the analytical reproducibility is not significant in terms of the overall variability, and secondly, it needs to be established over what field area a particular elemental analysis represents the concentration of that element for the sample as taken.

In this work, the components of variability associated with partial extractions of soils over glaciolacustrine clay-covered blind Ni mineralization, are isolated and evaluated for particular sample media, grain size fractions, and extraction types to determine major components of variability. The results of composite sampling, which was employed to reduce major components of variability to obtain more meaningful anomaly patterns, are subsequently presented as profiles. The final section focuses on the underlying sources of variability that are responsible for erratic Type 2 anomaly patterns.
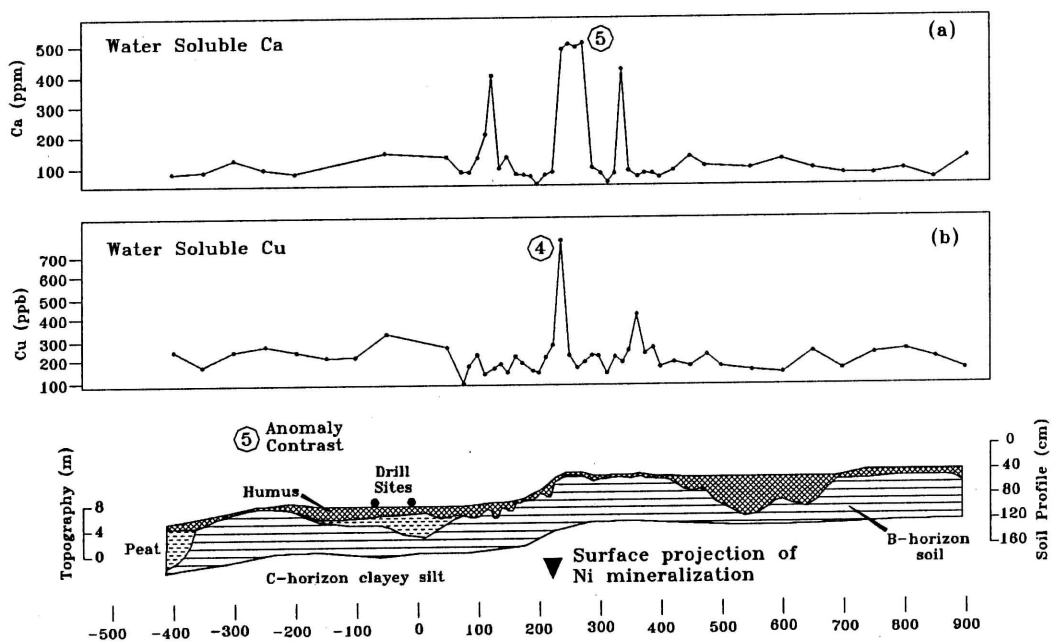

Figure 2. Distribution of water-soluble Ca (a) and Cu (b) in B-horizon soils over clay-covered blind Ni mineralization in northern Manitoba. The Type 1 anomaly (a) is typified by anomalous Ca in four consecutive samples adjacent to mineralization. The Type 2 anomaly (b) is characterized by anomalous Cu in one sample directly over the mineralization. More confidence is placed in the Type 1 anomaly (Seneshen, 1997).

2.0 Definition of Variability Components

The components of variability in geochemical data are given in equation 2.1 (modified after Thompson, 1992). This expression simply states that the total variance in the system is equal to the between sample site variance (S^2_{BSite}) plus variations associated with the sample site (S^2_{WSite}), sample ($S^2_{WSample}$), and the analytical procedure ($S^2_{Analytical}$). The term S^2 is somewhat of a misnomer because it is actually the sums of squares (SS) that are added or subtracted, and not the variance itself. In other work, the variance within individual field samples is considered (Thompson, 1992), but an estimation of the variance within sample sites is also necessary to determine effective sample intervals.

$$(2.1)\ S^2_{Total} = S^2_{Bsite} + (S^2_{Wsite} + S^2_{Wsample} + S^2_{Analytical})$$

(2.1) Analytical Variance ($S^2_{Analytical}$)

The analytical variability expresses the reproducibility of the analytical procedures. Also inherent in this expression is the homogeneity of a particular reference material with respect to a particular element. In this work, the variance was assessed by the replicate analysis of international standards and secondary reference materials; the latter were developed in house. The reference materials were included at regular intervals in analytical batches of field samples. However, in many of the analytical batches, the element contents of these reference materials did not extend over the concentration range of the associated field samples. For this reason, the analytical variance was also monitored using analytical duplicates that were prepared by taking splits of processed (i.e. dried and sieved) humus, B-horizon soils, and C-horizon parent material (Fig. 3). In most cases, the element contents of the analytical duplicates extend over the concentration range of the field samples, and the variability found using the duplicates is equal to, or lower than, the variability associated with the reference materials.

The analytical relative standard deviation (RSD) is taken as a measure of how well mean element concentrations of samples can be estimated at the analytical stage on the basis of replicate or duplicate analysis. The RSD is a measure of the relative precision defined as the standard deviation divided by the sample mean. In other words, if a particular sample that is analysed in replicate gives a mean concentration 200 ppm Zn, an RSD of 10 would signify a precision of +/-10% or +/-20 ppm. In this work, relative standard deviations for all components of variability are calculated at the 95% confidence level which means that, in the example given, repeated analyses of the sample would result in concentrations that are between 180 and 220 ppm 95 times out of 100.

(2.2) Interbatch Variance

The interbatch variance is a measure of the consistency in the laboratories with respect to sample preparation (e.g. weighing), extraction, and analytical procedures over time, (i.e. the laboratories ability to reproduce their analytical results analysing the same samples). It was assessed by re-analysing processed samples (i.e. dried and sieved) and standards at different times throughout the study.
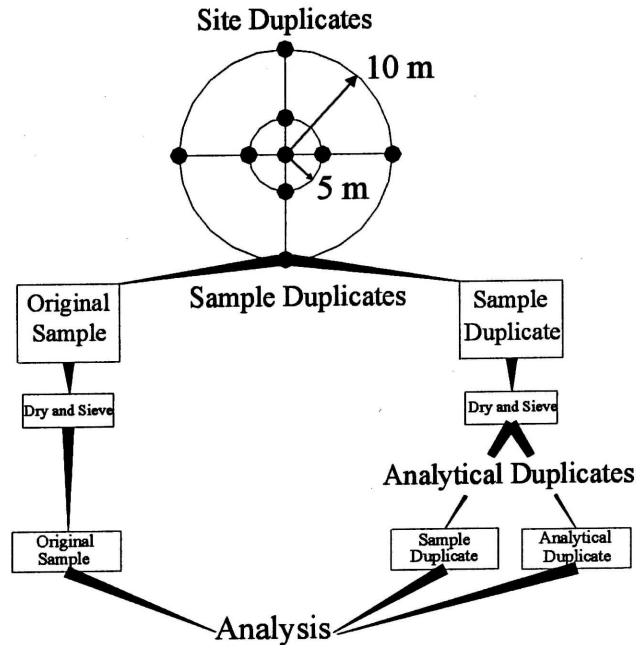
4

Figure 3. Procedures for the collection of site duplicates and the preparation of sample and analytical duplicates. The duplicates were used to estimate the components of variability associated with the use of partial extractions on various sample media.

(2.3) Within Sample Variance ($S^2_{WSample}$)

In this study, 1-kg organic and inorganic field samples were collected for partial extraction analysis. A 0.25-g (i.e. for Aqua Regia) to 1-g (i.e. for Enzyme Leach) aliquot is used for partial extraction analysis, and the element concentrations reported are assumed to be representative of the 1 kg field sample.

The sample representivity can be estimated using the sample variability, which is a measure of the homogeneity within the 1-kg field samples that were collected from different media and analysed by various partial extractions. It was monitored using <u>sample</u> duplicates that were prepared by drying, sieving, and analysing 100-g sub-samples from the 1-kg field samples (Fig. 3).

(2.4) Within Site Variance (S^2_{WSite})

If field samples are collected at 10-m intervals, the total area of the sample site can be represented by a 20-m diameter circle. Assuming an average vertical sample interval of 20 cm and an average soil density of 1.2 g/cm^3, then the total mass of soil available for sampling at the site is 75,000,000 g. It is assumed that the 1000 g field sample, is representative of the total mass of soil at the site, and furthermore, that the 0.25 to 1-gram sub-sample taken for partial extraction analysis is also representative of the 75,000,000 g of soil. The 1-gram sub-sample used in the enzyme leach comprises a very small proportion (13 x 10^{-7}%) of the sample site,

and the representivity of the sample sites, or indeed the field samples themselves, is therefore of serious concern.

The sample representivity associated with the glacial overburden was monitored using site duplicates (Fig. 3). The duplicates were collected at 5 and 10-m intervals around center samples at successive sites along a traverse or at discrete sites over mineralization and background areas.

(2.5) Between Site Variance (S^2_{BSite})

The between site variance is the "natural" or "true" variation in mean element concentration between the sample sites. To realise this "natural variation", it is necessary to subtract the contributions made by the analytical and sampling components from the total variance as indicated in equation 2.2. Natural variations in element concentrations between sample sites reveal the "true anomaly pattern" associated with a particular sample media and extraction type.

$$(2.2) \ S^2_{Bsite} = S^2_{Total} - (S^2_{WSite} + S^2_{WSample} + S^2_{Analytical})$$

(2.6) Total Variance (S^2_{Total})

The total variance is the sum of natural or between sample site (S^2_{Bsite}) variance and the background variations associated with the sample site (S^2_{WSite}), sample ($S^2_{WSample}$), and analysis ($S^2_{Analytical}$). In this work, it is the variance of all samples about the grand mean of the data for a particular area.

(3.0) Variability in glaciolacustrine clay that covers blind Ni mineralization

The anomaly patterns shown by aqua regia extractable elements in the A-horizon soils, and aqua regia and enzyme extractable elements in the B-horizon soils over clay-covered Ni mineralization in northern Manitoba are very erratic (Fig. 4). The total variability associated with strong and weak extractable elements in the soils was decomposed to determine the major component(s) of variability that is responsible for the erratic anomaly patterns.

(3.1) A-horizon soils (Strong Extraction)

The analytical variability for most elements of interest is acceptably low (<5%), and this is taken to imply good consistency in the digestion and analytical procedures (Table 1a). The analytical duplicates show similar variability to the lake sediment reference materials (LKSD). Therefore, they are taken to be as homogeneous for a 0.25-g aliquot as the reference materials, and they can be considered as suitable substitutes for assessing analytical variability. The interbatch variability is also acceptably low (<10%) signifying consistent digestion and analytical procedures over longer time periods.
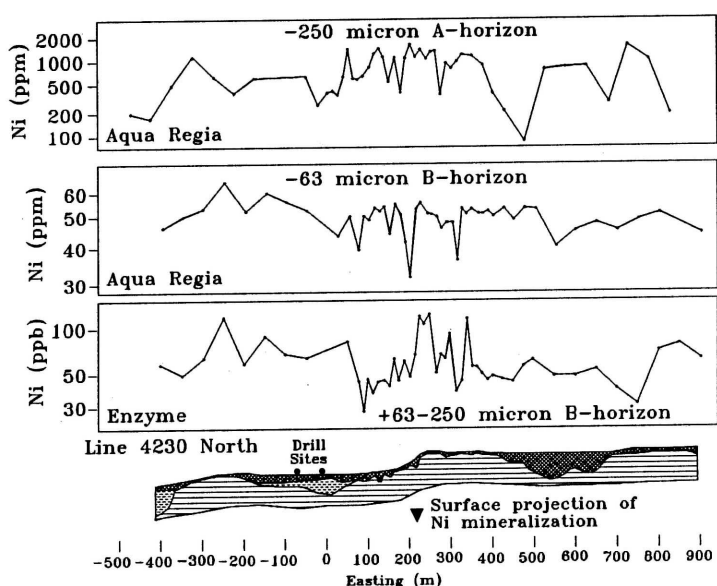
The within site variability shown by A-horizon soils is considerably higher than the analytical variability, and it is similar in magnitude to the total variability (Table 1a). This implies considerable heterogeneity of the elements and their source minerals within the 20-m diameter sample sites from which site duplicates were collected.

(3.2) B-horizon Soils and C-horizon Clayey Silt (Strong Extraction)

As for the A-horizon soils, the analytical variability shown by B-horizon duplicates and reference materials is negligible compared with the total variability (Table 1b). The higher analytical variability shown by Co and Ni in the standards reflects near detection limit levels of these elements. The benefit of assessing analytical variability through the use of analytical duplicates that have similar matrices and concentration ranges compared with the majority of samples being analysed is emphasized.

The interbatch variability is generally low (<5%) for most elements, but it is higher for Cu (16%) suggesting either inconsistency in laboratory procedures or innate problems for this element (Table 1b). The analytical and within sample variability are nearly equal which indicates good homogeneity within the samples (i.e. for 1 g aliquots taken from a 1 kg field sample).

Figure 4. Distribution of aqua regia extractable Ni (A-horizon), and aqua regia and enzyme extractable Ni

(B-horizon) over one of three lines samples above clay-covered Ni mineralization in northern Manitoba.

As for the A-horizon soils, the within site variability shown by aqua regia extractable elements in B-horizon soils greatly exceeds (4 to 8 times) that of the sample or analysis, and it is more similar to the total variability indicating significant within site variation (Table 1b).

Table 1. Relative Standard Deviations (%) that express the magnitude of total, within site, within sample, analytical, and interbatch variability for aqua regia and enzyme extractable elements in A- and B-horizon soils, and C-horizon parent material over clay-covered Ni mineralization in northern Manitoba.

(a)	-250 µm A-horizon Soils (Aqua Regia Extraction)				
Element	Mn	Fe	Co	Ni	Cu
Total Variability (n=331)	76	48	50	33	48
Site Variability (n=128)	42	44	36	23	37
Analytical Variability (Duplicates, n=50)	2	5	5	2	2
Analytical Variability (Standards, n=20)	3	3	3	2	3
Interbatch Variability (n=20)	4	10	3	3	3

(b)	-63 µm B-horizon Soils (Aqua Regia Extraction)				
Element	Mn	Fe	Co	Ni	Cu
Total Variability (n=331)	15	20	20	18	28
Site Variability (n=128)	11	12	12	13	17
Sample Variability (n=50)	1	1	3	2	2
Analytical Variability (Duplicates, n=50)	2	2	4	2	2
Analytical Variability (Standards, n=20)	6	4	9	6	4
Interbatch Variability (n=20)	2	5	3	3	16

(c)	-63 µm C-horizon Clayey Silt (Aqua Regia Extraction)				
Element	Mn	Fe	Co	Ni	Cu
Total Variability (n=331)	17	21	23	18	25
Site Variability (n=128)	8	7	10	6	7
Sample Variability (n=50)	1	1	2	2	1
Analytical Variability (Duplicates, n=50)	2	2	3	2	2

(d)	-63 µm B-horizon Soils (Enzyme Leach)				
Element	Mn	Fe	Co	Ni	Cu
Total Variability (n=331)	48	51	40	47	39
Site Variability (n=128)	39	44	32	44	39
Sample Variability (n=50)	7	14	5	6	36
Analytical Variability (Duplicates, n=50)	4	10	4	5	22
Analytical Variability (Standards, n=20)	11	8	7	12	20
Interbatch Variability (n=20)	7	10	10	18	20

(e)	-63 µm C-horizon Clayey Silt (Enzyme Leach)				
Element	Mn	Fe	Co	Ni	Cu
Total Variability (n=331)	35	44	34	30	27
Site Variability (n=128)	33	33	34	30	15
Sample Variability (n=50)	3	6	3	6	10
Analytical Variability (Duplicates, n=50)	4	8	4	6	8

In comparison with the B-horizon soils, the aqua regia extractable elements in the C-horizon show similar analytical and within sample variability (Table 1c). However, the within site variability is 1.5 to 2.5 times lower in the C-horizon which signifies a more uniform distribution of aqua regia extractable elements and their source minerals in the parent material.

(3.3) B-horizon Soils and C-horizon Clayey Silt (Weak Extraction)

The analytical variability shown by the enzyme extractable Mn, Co, and Ni in the B-horizon soils is comparable with that of the aqua regia extractable Mn, Co, and Ni, but it is 5 times higher for Fe and 11 times higher for Cu implying lower reproducibility for these elements, and more heterogeneity of Fe and Cu and their source minerals within the dried and sieved analytical duplicates (Table 1d).

In comparison with the analytical variability, the interbatch variability shown by enzyme extractable elements in B-horizon soils is of similar magnitude to that of the Mn and Fe, but it is 2 to 3.5 times higher for Co and Ni. It is difficult to assign a reason for this, but it would appear to be related to the analytical equipment rather than to sample preparation procedures; the latter being common for all elements. In comparison with the aqua regia extraction, the interbatch variability shown by the enzyme extraction is 2 to 9 times higher for all elements (Table 1d), which would be expected considering that element concentrations are three orders of magnitude lower.

The within sample variability associated with the enzyme leach is 2 to 18 times higher for Mn, Fe, Co, Ni, and Cu than that shown by corresponding aqua regia extractable elements, and it is particularly high for Fe and Cu, indicating that the elements and their source minerals are erratically distributed within the individual 1 kg field samples (Table 1d).

In comparison with the aqua regia site variability, the variability shown by all enzyme extractable elements is 3 to 4 times higher, and it comprises a greater percentage of the total variability; this relationship applies to the A-, B-, and C-horizon samples (cf. Tables 1 a, b, c, d, e). This signifies that these elements are more erratically distributed between site duplicates with respect to the enzyme leach, and this is a reflection of the irregular distribution of their source minerals (i.e. Mn-oxides) within the 20-m diameter sample sites. In such situations, the true anomaly pattern is concealed by this noise, and the anomaly patterns are consequently erratic and difficult to interpret.

The analytical and within sample variability for enzyme extractable Mn, Fe, Co, and Cu in the C-horizon parent material is half to one third of the same elements in the B-horizon, which implies a more uniform distribution of these elements in the C-horizon (cf. Tables 1 d and e). There is no decrease in the analytical or within sample variability observed for Ni between the horizons. In comparison with the analytical and within sample variability shown by aqua regia extractable elements in the C-horizon, that shown by corresponding enzyme extractable elements is 2 to 4 times higher.

The within site variability of enzyme extractable Fe, Ni, and Cu in the C-horizon shows a 1.5 to 2.5 fold decrease relative to corresponding elements in the B-horizon, implying a more homogeneous distribution of these elements and their source minerals in the C-horizon parent material (cf. Tables 1 d and e). The variability shown by Co and Mn does not change significantly between the horizons. In comparison with the site variability of

aqua regia extractable elements in the C-horizon, that of corresponding enzyme extractable elements is 2 to 5 times higher (cf. Tables 1 c and e).

(4.0) Reduction of Site Variability by Composite Sampling

The investigation indicates that both the analytical and sample variability comprise a small part of the total variability for the most part. The major component of variability is associated with the sample site itself. The high site variability is depicted in Figure 5, which shows the distribution of enzyme extractable Ni in B-horizon soil and C-horizon clayey silt over the blind Ni mineralization and background areas. It is apparent from the diagram that it would be difficult repeat anomalous responses within the 20-m diameter sample sites over mineralization. It would be impractical from a cost standpoint to collect and analyse multiple samples from the sites for the purpose of averaging element concentrations to obtain more uniform anomaly patterns. However, multiple samples could be blended together for one analysis per site to achieve more representative patterns.

The data are presented in graphical form as single element plots that compare the anomaly patterns of point and composite samples. The term "point" refers to the sample at the centre of sample sites, but "composite" refers to the sample that was prepared by blending the point sample and eight duplicates around it from each site (Fig. 5). The composites were prepared by blending nine unprocessed samples (i.e. not dried or sieved) from each site, and the blended sample from each site was then dried and sieved for aqua regia and enzyme extractions.

(4.1) A-horizon Soils (Strong Extraction)

The aqua regia analysis of composite samples produces a more uniform anomaly pattern compared with the point samples (Fig. 6). The Ni is anomalous 80 m up-ice of the buried mineralization, but its concentration level is equivalent to that over background between -225 and -275 East. It is therefore improbable that the anomaly is indicative of mineralization. In essence, more representative patterns can be realised by analysing A-horizon composite samples, but the more uniform patterns do not necessarily reflect mineralization.

(4.2) B-horizon Soils (Strong Extraction)

The point and composite samples show the same anomaly pattern because of the low site variability associated with aqua regia extractable Ni (Fig. 6). In other words, the pattern shown by the point samples represents the natural variation in the Ni concentration between sites (i.e. a good approximation of mean concentration), and composite samples are therefore not required. There is a low contrast anomaly 50 m up-ice of the mineralization, but this probably reflects subtle variations in the abundance of source minerals of aqua regia extractable Ni (e.g. chlorite).
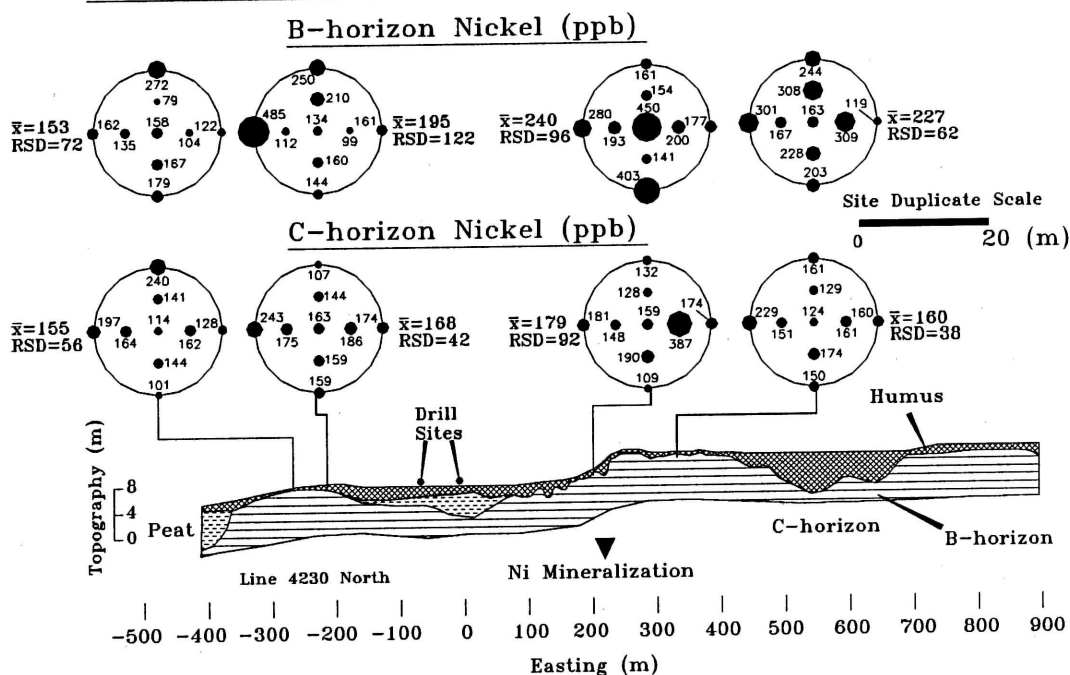
Figure 5. Distribution of enzyme extractable Ni (-63 μm B-horizon soil and C-horizon clayey silt) within 20- m diameter sample sites over Ni mineralization and background areas in northern Manitoba.

(4.3) B-horizon Soils (Weak Extraction)

The composite samples produce a more uniform anomaly pattern for enzyme extractable Ni compared with the point samples, and both types of composite samples reveal a low contrast, multi-point Ni anomaly immediately down-ice of the mineralization between 150 and 200 East (Fig. 6). The Ni is anomalous in three adjacent samples but because of the high site variability shown by enzyme extractable Ni in B-horizon soils (Table 1d), it would be difficult to regard this anomaly as statistically significant with composites made from only nine samples per site.
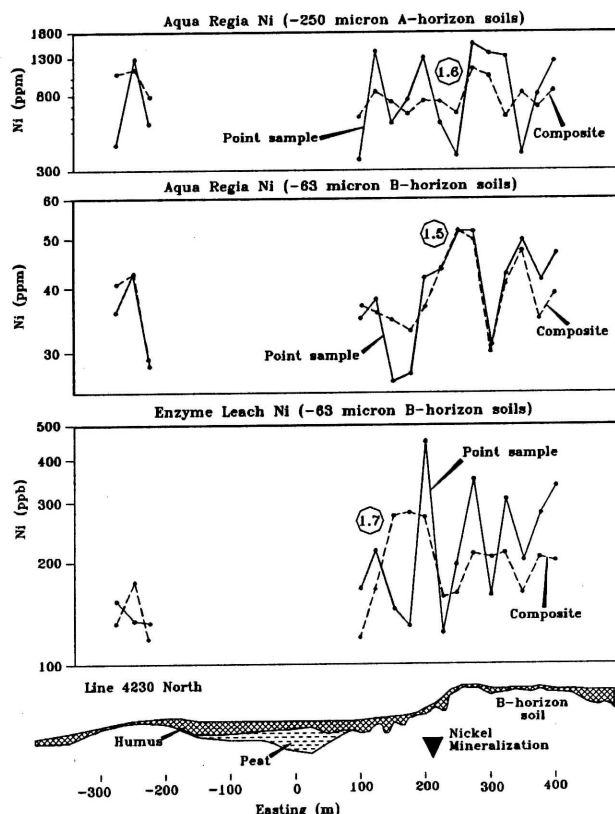
Figure 6. Distribution of aqua regia extractable Ni (A- and B-horizons) and enzyme extractable Ni (B-horizon) in point and composite samples over clay-covered blind Ni mineralization in northern Manitoba.

(5.0) Sources of variability associated with the use of partial extractions

(5.1) Analysis

The use of reference and/or sieve duplicates for monitoring the analytical variability associated with weak extractions is essential for meaningful interpretation of the data. Table 2 provides the results of the replicate analysis (weak extraction) of an international podzolic soil standard (i.e. SO-2). Significant fluctuations in Ni and Cu concentrations are evident in the replicates throughout the batch of 950 field samples. The downward, or less frequent upward shifts in element concentration, are non-uniform and they occur at different levels in the batch. It is difficult to assign a reason for these non-uniform changes in the Ni and Cu concentration throughout the analytical batch, but it could relate to the use of internal standards that do not perform a uniform correction for particular elements to account for drift on the ICP-MS. In addition to the non-uniform shifts in element concentration, there can be "carry over" effects within a batch of field samples as shown in Figure 7. This occurs in batches where there are extreme variations in element concentration between successive samples. Insufficient washing with dilute acid between analyses results in the build-up of elements on the cones of the ICP-MS, and this material is carried over to successive samples.

12

Table 2. Results of replicate weak extraction analysis of the S0-2 podzol within a batch of 950 field samples.

Sample Number	Ni	Cu
20	38	2.5
60	31	7
100	28	6
140	2.5	2.5
181	38	2.5
220	40	2.5
262	39	2.5
301	41	2.5
340	2.5	2.5
380	2.5	2.5
420	2.5	2.5
461	2.5	2.5
500	2.5	2.5
540	2.5	2.5
580	34	13
620	39	11
660	38	18
701	44	21
741	37	213
781	37	11
821	37	14
861	40	13
901	37	13

It is essential that laboratories are made aware of these problems with analytical procedures. They appreciate the insight into these problems, and they are more than willing to rectify procedures and re-analyse batches with satisfactory results.

(5.2) Sample Processing

A sample processing experiment was designed to test the effects of different types and quality of contamination introduced by processing on enzyme leach results. It was also decided to test the effects of drying temperature on results in the same experiment.

Three B-horizon soil samples were selected from both background and mineralized areas on the basis of visual homogeneity and similar trace element concentration range. The soils chosen consist of variable proportions of subangular to subrounded, Fe-oxide coated, granitic and mafic volcanic rock fragments in a matrix composed largely of clear, subangular quartz, lesser Fe-oxide coated plagioclase, and minor clinochlore, tremolite, and woody organic matter. A 15 to 25 gram sub-sample of each of the B-horizon samples was dried at 25^0C for 26 hours; every sub-sample was analysed in duplicate. The experiment was repeated at five other temperatures, which ranged from 30 to 143^0C. Following drying, all sub-samples were sieved to three grain size fractions (-125, -177, and -250 μm), and analytical duplicates were taken randomly from five of the six batches.
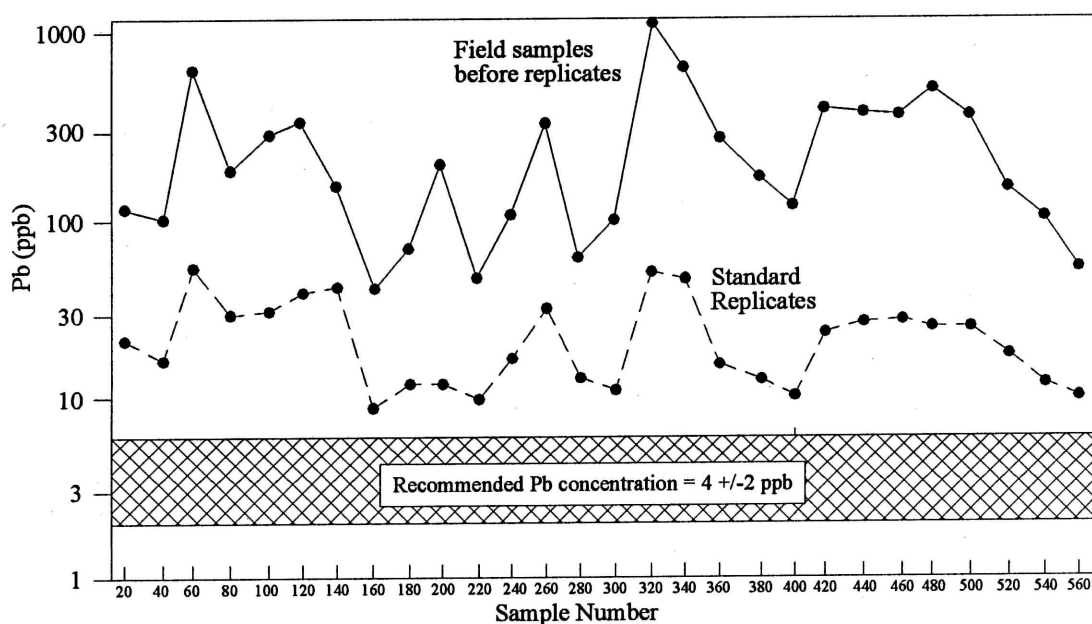
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Figure 7. Weak extractable Pb content of standard replicates and the field samples that immediately preceded them in the analytical batch of 600 samples. The strong correlation of Pb between the standards and field samples suggests that Pb is being "carried over" to the replicates because of insufficient washes between successive analyses.

(5.21) Effect of Variable Drying Temperature on Results

The three size fractions of the B-horizon soils showed no significant change in enzyme extractable element concentrations by drying at 25^0, 30^0, 36^0, or 45^0C. However, for sample 895, there is an approximate 4-fold increase in the Cu concentration for all size fractions by drying at 70^0C (Fig. 8a). A further 2 to 3-fold increase in Cu concentration occurred between 70^0 and 143^0C. The other two samples showed only moderate (~1.5 to 2 fold) increase in Cu concentration between 45^0 and 70^0C, and a minor increase (1.3 fold) from 70^0 to 143^0C. Above 45^0C sample 905 did not show significant differences in Cu concentration between size fractions as did samples 829 and 895. The enzyme extractable Br shows considerably larger increases in concentration than Cu with higher drying temperature (Fig. 8b). All three samples indicate a 10-fold increase in the Br concentration between 45^0 and 70^0C, but the relationship between the grain size fractions is similar to that shown by Cu. With the exception of Rb, which showed a decrease in concentration with drying temperature, all of the other enzyme extractable elements showed considerable, non-uniform increases in concentration with drying temperature. The non-uniform increase in element concentration as a result of drying samples at temperatures above 45^0C would therefore introduce considerable variability into enzyme leach results.

It is difficult to assign reasons for the increase in enzyme extractable element concentrations with increasing drying temperature, but possible causes could be: (1) micaceous minerals (e.g. vermiculite, smectite) expanded by excessive heating to expose

14

interlayer cations and anions to the enzyme leach solution, and/or (2) the transformation of amorphous Fe-oxides to crystalline maghemite during heating caused the outward migration of trace elements to grain surfaces making them more susceptible to enzyme leach dissolution. This outward mobilization of trace elements from Fe-oxides has been observed in Australian lag gravels that underwent excessive heating during bush fires.
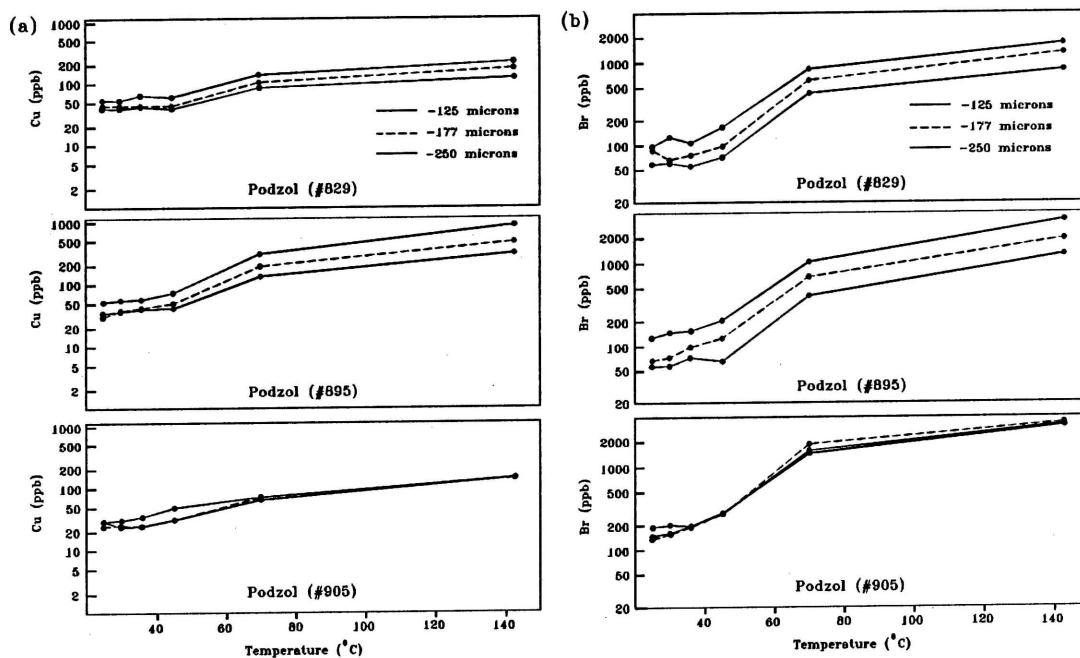

Figure 8. Plots of enzyme extractable Cu (a) and Br (b) versus drying temperature for three grain size fractions of podzolic B-horizon soils over till-covered Zn mineralization in northern Quebec (Seneshen, 1997).

(5.22) Effects of Contamination on Results

The enzyme leach extracts about 1% of aqua regia extractable trace elements from B-horizon soils and parent material, and all elements are reported at the parts per billion level. At these concentration levels, there is significant potential for contamination of samples from a variety of sources. Possible contaminant sources that were tested using silica sand of known composition as a blank, included kraft paper bags, plastic, stainless steel and brass sieves, and suntan lotion. Of the contaminant sources tested, only those involving kraft paper bags, brass sieves, and possibly suntan lotion introduced significant contamination to the enzyme leach results (Table 3).

Contamination from Paper Sample Bags

Kraft paper bags are commonly used in soil and stream sediment surveys because they are durable, waterproof, compact, and can hold considerable volumes of soil or sediment. However, these bags were suspected to be a possible source of Zn contamination with respect to enzyme extractions. To test this concept, silica sand was saturated with deionized water in a

15

glass cake dish, and sub-samples split into separate paper bags with a stainless steel spoon prior to drying at a specific temperature over a fixed time interval (26 hours); the temperatures used were 30^0, 45^0C, and 70^0C. The deionized water, which was analysed by ICP-MS, was found to contain less than detection limit (<5 ppb) levels of Zn and Cu.

Table 3. Mean enzyme extractable Cu and Zn contents (ppb) of silica sand and probable contaminant sources.

Sample Type	Statistics	Cu (ppb)	Zn (ppb)
Original Silica Sand Not dried (n=12)	Mean Standard Deviation	83 5	451 23
Silica Sand Dried in Kraft Paper Bags Dried at 30°C (n=4)	Mean Standard Deviation	67 3	1910 580
Suntan Lotion Added to Silica Sand Dried at 30°C (n=4)	Mean Standard Deviation	57 8	1429 402
Silica Sand Screened in Brass Sieves Dried (n=1)	Mean	2147	1029

The treated silica sand, dried at 30^0C, showed a 4 fold increase in mean Zn and 1.2 fold decrease in mean Cu relative to the same un-treated silica sand (Table 3). The sample dried at 70^0C, was found to contain 200 ppb more Zn than samples dried at 30^0 and 45^0C. Follow-up work, which consisted of HNO_3 digestion and multi-element ICP-ES analysis of various parts of the bags, indicated that most of the Zn was derived from the glue in the seam of the bags which contained up to 900 ppm Zn.

It is speculated that some of the Zn was dissolved in deionized water as Zn^{2+}, and then precipitated, possibly as a hydroxide (i.e. $ZnOH_2$) during evaporation of the water. The Zn contamination from paper bags was recognized in the first year (i.e. 1993) of the investigation, and the majority of samples for the study were collected in plastic zip-loc bags during the remainder of the program. The reason(s) for the slight decrease in Cu contents from the original silica sand to the treated samples is unknown.

Contamination from Sieves

Detection limits for a strong extraction and ICP-ES analysis of soils are generally in the low ppm range, and the addition of 1 to 2 ppm Zn or Cu from a particular sieve will therefore not have a profound effect on results. On the other hand, the addition of 1000 to 2000 ppb Zn or Cu from sieves could dramatically influence the interpretation of enzyme leach results.

To evaluate the input of contaminants from sieves, 300-gram splits of silica sand were placed in a -250 μm, plastic sieve with nylon mesh, and shaken on a Fisher sieve shaker for 15 minutes. The experiment was repeated using stainless steel and brass sieves. There was no

contamination from either the plastic/nylon or the stainless steel sieves, but the silica sand screened in brass sieves, showed a more than 20 fold increase in Cu and a 2 fold increase in Zn (Table 3). These metals may occur as soluble hydroxides on the brass sieves, and are thus susceptible to dissolution by the aqueous-based enzyme leach.

Contamination from Suntan Lotion

Suntan lotion is generally applied prior to sampling in the field to prevent sunburn. As suntan lotion contains considerable quantities of Zn-oxide, it was suspected as a potential contaminant. In the example given, 20 to 30 ml of Coppertone (15) suntan lotion were mixed into 21 to 24 grams of silica sand. The sample was then dried in paper bags at 36^0C for 26 hours, split into four samples, and submitted for enzyme leach analysis.

The results indicated a 3-fold increase in mean Zn concentration relative to the original silica sand (Table 3). Unfortunately, the input of Zn from paper bags was not known at the time of testing, and thus, the amount of Zn contributed from suntan lotion relative to paper bags remains unknown. However, the effect of suntan lotion on enzyme extractable Zn concentrations could be tested in a future experiment by mixing suntan lotion and silica sand, and allowing it to air dry in a glass dish prior to enzyme analysis.

(5.3) Mineralogical Variations

It was established in Section 3 that the main component of variability responsible for irregular anomaly patterns is associated mainly with the sample site rather than the sample or analysis. This suggests that strong and weak extractable elements are associated with source minerals that are erratically distributed within sample sites and, in some cases, within the 1-kg field samples. So what are these source minerals? What causes their irregular distribution over short distances?

In order to determine the types of source minerals susceptible to attack by partial extractions, certified reference materials and blanks (i.e. silica sand) were subjected to partial extractions of variable strength. Certified inorganic (i.e. S0-2 podzol) and organic (i.e. orchard leaves) reference materials were analysed for enzyme and aqua regia extractable elements. Silica sand was also included in the analysis as a blank to establish base line element concentrations to compare with the standards.

It is important to note that when examining the data, it is the percentage of enzyme to aqua regia extractable metal that provides clues as to the form of source minerals (Table 4). For example, all media tested contain low amounts (<1%) of enzyme extractable Fe, but the silica sand and orchard leaves contain considerably more enzyme extractable Mn and Zn than the B-horizon podzolic soil. Assuming that the silica sand contains little or no sesquioxides, then the aqueous-based enzyme leach must be dissolving water-soluble forms of Mn and Zn. In a similar sense, the orchard leaves presumably contain minimal sesquioxides for reduction and dissolution by the enzyme leach. The large amount of enzyme extractable Mn and Zn must

17

therefore be derived from the oxidative breakdown of organic matter. This seems logical since the enzyme leach uses H_2O_2 that is capable of oxidizing organic matter. In the case of SO-2, the enzyme extractable Mn and Zn is probably largely derived from amorphous Mn-oxides because this is commonly a significant component of podzolic soils. From the examination of the data it can be concluded that enzyme extractable elements are derived water-soluble phases, sesquioxides, and organic matter. So what controls the distribution of these source minerals in nature? The answer to this question is beyond the scope of this workshop, but some possibilities can be given.

Table 4. Mean enzyme extractable metal contents (ppb) of silica sand and certified reference materials. The percentage extracted relative to the aqua regia extractable element concentration is given in brackets.

Sample Type	Mn	Fe	Zn
Silica Sand (n=12)	117 (16%)	750 (0.13%)	451 (12%)
Inorganic Standard (SO-2) (n=10)	2490 (1.78%)	40233 (0.43%)	483 (1.01%)
Organic Standard (Orchard Leaves) (n=10)	51520 (96%)	4500 (0.99%)	9701 (33%)

Variation in the spatial distribution of source minerals could be caused by local changes in terrain conditions. For example, the amount of amorphous Mn-held Co increases dramatically in elevated areas of the line sampled over clay-covered Ni mineralization in northern Manitoba (Fig. 9). In these areas, the A-horizon soils are considerably thinner which could allow the ingress of more oxygen to the B-horizon soils. This would promote the co-precipitation of Mn and Co from groundwater. The grain size distribution of soils also controls the distribution of enzyme extractable elements, and this aspect will be further discussed in the workshop.
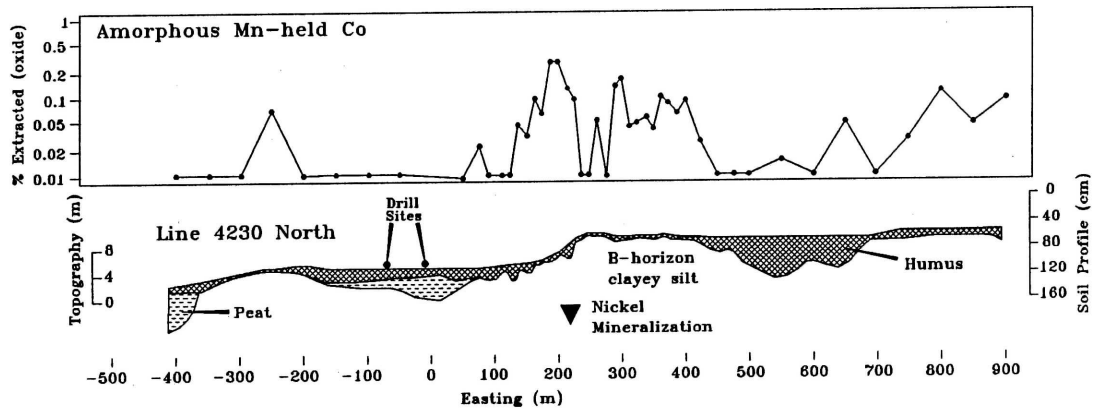
Figure 9. Distribution of amorphous Mn-held Co in B-horizon soils over clay-covered Ni mineralization in northern Manitoba. The Co increases in elevated areas with thinA-horizon soils and this could reflect the ingress of more oxygen to B-horizon soils in these areas that would promote the co-precipitation of Mn and Co.

(6.0) Conclusions

The following conclusions can be drawn from this investigation into the variability associated with the use of partial extractions:

(1) Erratic anomaly patterns that consist of isolated single-point anomalies are mainly related to high site and sample variability that is a reflection of the irregular distribution of source minerals over short distances. The distribution of source minerals appears to be influenced by changes in local terrain conditions that directly effects soil composition (e.g. organic carbon content), grain size composition, and redox conditions.

(2) More uniform and meaningful anomaly patterns can be obtained by composite sampling of A- and B-horizon soils, particularly in the case of weak extractions.

(3) More care must be devoted to sample processing and analysis, particularly for weak extractions, to prevent the occurrence of spurious anomalies.

19

Acknowledgements

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<u>Appendix 1. Results of forty-eight studies that tested partial extractions of variable strength in different types of transported overburden</u>

(1.1) Twelve CHIM Case Studies

(1.2) Three Hydroxylamine HCl Case Studies

(1.3) Five Thermomagnetic Geochemical Method (TMGM) Case Studies

(1.4) Twelve Na-Pyrophosphate (MPF) Case Studies

(1.5) Twelve Enzyme Leach Case Studies

(1.6) Four Deionized Water Leach Case Studies

Table 1.1 CHIM Case Studies (*Anomaly contrast is the signal to noise ratio)

Property	Location	Overburden	Mineralization	Comments	Reference
Gorevskoe	Kazakhstan	15-20 m sandy clay	Steeply dipping Pb-Zn orebodies in limestone; 5-7% Pb-Zn in orebody A; 10% Pb, 0.25% Zn in orebody B	Single-point Pb and Zn anomalies over orebody A; only a single-sample Pb anomaly over orebody B *Anomaly contrast = 6 to 8	Alekseev et al. (1996)
Semiletka	Kola Peninsula	10-20 m morainic deposits	Moderately dipping Cu-Ni ores (<5% Cu + Ni)	Single-point Cu anomaly directly over mineralization Anomaly contrast = 6	Alekseev et al. (1996)
Belorussia	Belorussia	>40 m unconsolidated overburden and bedrock	Flat-lying REE mineralization within a diabase dyke and metasomatized granite	Multi-point Be anomaly directly over mineralization; second CHIM anomaly further along the line was drilled and additional mineralization was discovered Anomaly contrast = 3 to 5	Antropova et al. (1992)
Lishui	Jiangsu Province, China	5 m alluvium	Steeply dipping 1-15 m wide orebody comprised of auriferous sulphide-bearing quartz veins in fractured breccia tuff; gold, electrum, and calaverite occur with pyrite in a gangue of quartz with minor sericite and barite	Single-point Au anomaly directly over the known Au vein Anomaly contrast = 5 Another multi-point CHIM anomaly on the line resulted in the discovery of another gold vein	Xu et al. (1989)
Wuhe	Anhui Province, China	2-4 m alluvium	Steeply dipping, 5 m wide free gold and sulphides in silicified fractures in Proterozoic granulite; gangue minerals are quartz, limonite and sericite	Single-point Au anomalies directly over steeply dipping veins Anomaly contrast = 8	Xu et al. (1989)
Fengyang	Anhui Province, China (30 km south-west of Wuhe Deposit	2-5 m alluvium	Shallow dipping, 0.8-1 m wide auriferous quartz veins in Proterozoic anorthosite; ore minerals are Au and pyrite; gangue is quartz	Single-point Au anomaly directly over subcrop of Au vein Anomaly contrast = 10	Xu et al. (1989)
Kokomo Mine	Russell Gulch, Colorado	1.8 m colluvium underlain by 0.9 m of weathered parent material	Steeply dipping, single 1 m wide Au-Pb-Zn bearing quartz vein; Pb-Zn mineralization was superimposed on earlier pyrite-Au mineralization	Single-point Cu anomaly and multi-point Zn anomaly directly over mineralization, but no Au anomaly Anomaly contrast = 10 to 20	Smith et al. (1993)

23

23

Table 1.1 (continued) CHIM Case Studies

Property	Location	Overburden	Mineralization	Comments	Reference
Aladahalli Main Block	Hassan District, Karnataka, Southern India	10 m residual soil over Precambrian schists The overburden is very poorly described	Subvertical lode zones (2-8 m) comprised of disseminated to semi-massive pyrite with minor pyrrhotite and chalcopyrite (1-2.5% Cu) in quartz-biotite-chlorite schist	Multi-point Zn, Cu, Pb anomalies directly over mineralization Anomaly contrast = 2 to 12 Conventional analytical methods (i.e. aqua regia) were not tested in this residual overburden	Talapatra et al. (1986)
Currie-Bowman	70 km due east of Timmins	0-35 m glaciolacustrine clays and silts overlying thin glaciofluvial sands and gravels; chalcopyrite in south-trending dispersion train for 2 km in basal gravels; no till present	Cu mineralization in argillite/volcani-clastic transition above footwall basalts; chalcopyrite replaces pyrite nodules or occurs as fracture coatings; sphalerite and galena-filled fractures along strike and below the Cu-mineralization	Noisy profiles for Cu, Zn, Pb, and Ag Single-point anomalies occur up- and down-ice of mineralization Cu and Pb anomalies appear to coincide with drill collars Anomaly contrast = 8	Ryss et al. (1990)
Wind-jammer	2.5 km south of Highway 101 midway between Matheson and the Quebec border	30-50 m Munro Esker sands and silts	Shallow to steep dipping, low sulphide, quartz-carbonate stock-works in altered basalts near Destor-Porcupine Fault or in iron formation/greywacke sequences	Noisy profiles for Au, Cu, Pb, and Zn with many single-sample peaks and troughs Au anomalies occur over and down-ice of mineralization making target definition very difficult Anomaly contrast = 4 to 6	Ryss et al. (1990)
Montcalm	70 km northwest of Timmins	10-40 m varved clays and gravelly sandy till; anomalous Ni in dispersion train down-ice of mineralization	4,200,000 tons @ 1.4% Ni, 0.7% Cu, 0.1% Co in two main and several minor lenses; semi-massive, net-textured, or disseminated pyrrhotite, pentlandite, and chalcopyrite; hosted in coarse-grained gabbro	Single-point Ni and Cu anomalies directly over or very proximal to subcropping mineralization Anomaly contrast = 4 to 6	Ryss et al. (1990) Hamilton et al. (1992)
Chance	30 km north of Timmins; 2 km northwest of Kidd Creek	30-55 m glaciolacustrine clays, glaciofluvial sands, and tills	200,000 tons @ 3% Pb, 13% Zn, 200 g/t Ag; 35m long, 5 m wide, plunges 85° west to a depth of 400 m where it is cut off by a fault	Single-point Zn, Cu, Pb, Ag, and M-factor anomalies directly over sub-cropping mineralization Anomaly contrast = 4 to 8 Weaker Zn anomaly over down-plunge blind portion of deposit to the west	Ryss et al. (1990) Hamilton et al. (1992)

24

Table 1.2 Hydroxylamine Hydrochloride Case Studies

Property	Location	Overburden	Mineralization	Comments	Reference
Xiao-Maoshan	Suzhou, Eastern China	40-50 m Quaternary transported overburden	Shallow dipping, polymetallic deposit	Low contrast, single-point Pb anomaly over part of the deposit Anomaly contrast = 2	Jin et al. (1989)
Montcalm	70 km northwest of Timmins	10-40 m varved clays and gravelly sandy till; anomalous Ni in dispersion train down-ice of mineralization	4,200,000 tons @ 1.4% Ni, 0.7% Cu, 0.1% Co in two main and several minor lenses; semi-massive, net-textured, or disseminated pyrrhotite, pentlandite, and chalcopyrite; hosted in coarse-grained gabbro	No response in Ni or Cu over mineralization, and no correlation with Russian TMGM	Hamilton et al. (1992)
Dundonald	50 km northeast of Timmins	0-41 m glaciofluvial gravelly sand and local glaciolacustrine silty sand lenses	**Dundeal Zone:** blebby and disseminated pyrrhotite-pentlandite with minor chalcopyrite and rare sphalerite at the base of a komatiite flow sequence (1.5-3.04% Ni) **Terminus Zone:** banded semi-massive to massive pyrrhotite with variable sphalerite and minor chalcopyrite in graphitic interflow argillite (2.5% Zn, 0.5% Cu)	Single-point Cu+Zn anomalies down-ice of the Terminus Zone on Lines 16+50W and 17+50W but these do not extend to L18+50W; Co+Ni increases in concentration southwards towards thinner overburden over gabbro subcrop Anomaly contrast = 3 to 6 **Aqua Regia** shows a multi-point Cu+Zn anomaly 100 m down-ice of Terminus Zone on L16+50W, and single-sample Cu+Zn anomalies up- and down-ice of mineralization on L17+50W; these anomalies do not extend to L18+50W Co+Ni levels are erratic with no spatial relationship to Dundeal Ni mineralization Anomaly contrast = 2	Hamilton et al. (1992) Seneshen (1997)

25

Table 1.3 Thermomagnetic Geochemical Method (TMGM) Case Studies

Property	Location	Overburden	Mineralization	Comments	Reference
Tin	Far East Russia	30 m Quaternary clays	Steeply dipping Sn mineralization in sandstone	High contrast, single-point Sn, Pb, Ag, and Sb anomalies over and around mineralization; however, there is no mention of Pb, Ag, or Sb in the mineralization Anomaly contrast = 2 to 20	Antropova et al. (1992)
Currie-Bowman	70 km due east of Timmins	0-35 m glaciolacustrine clays and silts overlying thin glaciofluvial sands and gravels; chalcopyrite in south-trending dispersion train for 2 km in basal gravels; no till present	Cu mineralization in argillite/volcaniclastic transition above footwall basalts; chalcopyrite replaces pyrite nodules or occurs as fracture coatings; sphalerite and galena-filled fractures along strike and below the Cu-mineralization	Single-point Cu*Zn*Pb anomalies over and down-ice of mineralization Anomaly contrast = 6	Ryss et al. (1990)
Chance	30 km north of Timmins 2 km north-west of Kidd Creek	30-55 m glaciolacustrine clays, glaciofluvial sands, and tills	200,000 tons @ 3% Pb, 13% Zn, 200 g/t Ag; orebody is 35 m long and 5 m wide and it plunges 85° west to a depth of 400 m where it is cut off by a fault	Multi-point Cu*Pb*Zn*Ag anomalies occur directly over base metal mineralization Anomaly contrast = 6 to 10	Ryss et al. (1990)
Montcalm	70 km northwest of Timmins	10-40 m varved clays and gravelly sandy till; anomalous Ni in dispersion train down-ice of mineralization	4,200,000 tons @ 1.4% Ni, 0.7% Cu, 0.1% Co in two main and several minor lenses; semi-massive, net-textured, or disseminated pyrrhotite, pentlandite, and chalcopyrite; hosted in coarse-grained gabrro	No response in Ni or Cu over mineralization	Ryss et al. (1990)
Wind-jammer	2.5 km south of Highway 101 midway between Matheson and the Quebec border	30-50 m Munro Esker sands and silts	Shallow to steep dipping, low sulphide, quartz- carbonate stock- works in altered basalts near Destor-Porcupine Fault or in iron formation/ greywacke sequences No mention of base metal sulphides	Single-point Cu*Pb*Zn*Ag anomalies occur over and down-ice of mineralization, but there is no mention of these elements in the ore Anomaly contrast = 4 to 10	Ryss et al. (1990)

26

Table 1.4 Na-pyrophosphate Extraction (MPF) Case Studies

Property	Location	Overburden	Mineralization	Comments	Reference
Semiletka	Kola Peninsula, Russia	10-20 m morainic deposits	Moderately dipping Cu-Ni ores (<5% Cu + Ni)	Multi-point Cu/C anomalies over and near mineralization Anomaly contrast = 5 to 8	Alekseev et al. (1996)
Rudny Altai	Rudny Altai, Russia	100-120 m unconsolidated clays overlain by loam overburden; up to 500 m barren bedrock	Shallow dipping polymetallic mineralization	Multi-point (Pb + Cu/C) anomaly directly over mineralization Anomaly contrast = 3	Antropova et al. (1992)
Zabarkalic	Zabaralic, Russia	40 m unconsolidated sediments	Flat-lying placer gold mineralization	Multi-point (Au/C * Ag/C * As/C) anomaly directly over mineralization Anomaly contrast = 14	Antropova et al. (1992)
Xixiashan	Suzhou, Eastern China	15-20 m Quaternary transported overburden 280 m barren sandstone	Steeply dipping Pb-Zn mineralization hosted in limestone	Single-point Ag, Hg, Pb, and Cu anomalies directly over mineralization Anomaly contrast = 6 to 30 Element concentrations are not normalized to organic carbon content in solution making interpretation difficult	Jin et al. (1989)
Xiaomaos-han	Suzhou, Eastern China	40-50 m Quaternary transported overburden	Shallow dipping, polymetallic deposit	Anomalies could not be interpreted due to lack of background data	Jin et al. (1989)
Currie-Bowman	70 km due east of Timmins	0-35 m glaciolacustrine clays and silts overlying thin glaciofluvial sands and gravels; chalcopyrite in south-trending dispersion train for 2 km in basal gravels; no till present	Cu mineralization in argillite/volcaniclastic transition above footwall basalts; chalcopyrite replaces pyrite nodules or occurs as fracture coatings; sphalerite and galena-filled fractures along strike and below the Cu-mineralization	Single-point Cu anomalies appear to be associated with drill collars rather than mineralization "Rabbit ear" zinc anomalies straddle mineralization but no response shown by Pb Anomaly contrast = 6 to 8	Ryss et al. (1990)
Wind-jammer	2.5 km south of Highway 101 midway between Matheson and the Quebec border	30-50 m Munro Esker gravelly sand	Shallow to steep dipping, low sulphide, auriferous, quartz-carbonate stock-works in altered basalts near Destor-Porcupine Fault or in iron formation/ greywacke sequences No mention of base metal sulphides	Single-point Cu/C*Pb/C*Zn/C anomalies occur near subvertical, volcanic- and sediment-hosted gold mineralization Anomaly contrast = 3 to 40 There is no mention of base metal concentration in mineralized zones given in the report and plots of Au and pathfinder elements (i.e. As) were not presented	Ryss et al. (1990)

27

Table 1.4 (continued) Na-pyrophosphate Extraction (MPF) Case Studies

Property	Location	Overburden	Mineralization	Comments	Reference
Chance	30 km north of Timmins 2 km northwest of Kidd Creek	30-55 m glaciolacustrine clays with minor intercalated glaciofluvial sand and till	200,000 tons @ 3% Pb, 13% Zn, 200 g/t Ag; 35m long, 5 m wide, plunges 85° west to a depth of 400 m where it is cut off by a fault	Single-point Cu/C, Zn/C, and Pb/C, and M-factor anomalies directly over mineralization Anomaly contrast = 400 to 800	Ryss et al. (1990) Hamilton et al. (1992)
Montcalm	70 km northwest of Timmins	10-40 m varved clays and minor gravelly sandy till anomalous Ni in dispersion train down-ice of mineralization	4,200,000 tons @ 1.4% Ni, 0.7% Cu, 0.1% Co in two main and several minor lenses; semi-massive, net-textured, or disseminated pyrrhotite, pentlandite, and chalcopyrite; hosted in coarse-grained gabbro	Single-point Ni anomaly directly over mineralization could not be reproduced by Hamilton et al. (1992) Anomaly contrast = 4	Ryss et al. (1990) Hamilton et al. (1992)
PK-Showing	Northern Quebec	0.8 to 2 m of poorly sorted basal till	Massive sulphide in interflow sediments (4.7% Zn/9.8 m)	Multi-point Cu anomaly over mineralization; same pattern as aqua regia Anomaly contrast =28	Seneshen (1997)
Clyde River	80 km southwest of Ottawa, Ontario	Less than 4 m of poorly sorted basal till	Narrow sphalerite lenses in dolomite; up to 17% Zn and 850 ppm Cd	Multi-point Zn anomaly over mineralization; same pattern as aqua regia Anomaly contrast =5	Seneshen (1997)
Dundonald	50 km northeast of Timmins	0-41 m glaciofluvial gravelly sand and local glaciolacustrine silty sand lenses	**Dundeal Zone:** blebby and disseminated pyrrhotite-pentlandite with minor chalcopyrite and rare sphalerite at the base of a komatiite flow sequence (1.5-3.04% Ni) **Terminus Zone:** banded semi-massive to massive pyrrhotite with variable sphalerite and minor chalcopyrite in graphitic interflow argillite (2.5% Zn, 0.5% Cu)	Raw data is noisy, but normalizing metals to carbon and adding ratios reveals low contrast (Cu/C+Zn/C) anomalies over and down-ice of Terminus Zone Co/C+Ni/C anomalies down-ice of Dundeal Zone probably reflect shallow gabbro subcrop Anomaly contrast = 2 to 10	Hamilton et al. (1992) Baird (1991) Seneshen (1997)

28

Table 1.5 Enzyme Leach Case Studies

Property	Location	Overburden	Mineralization	Comments	Reference
Kokomo Mine	Russell Gulch, Colorado	1.8 m colluvium underlain by 0.9 m of weathered parent material	Steeply dipping, single 1 m wide Au-Pb-Zn-Cu bearing quartz vein Pb-Zn-Cu mineralization was superimposed on earlier pyrite-Au mineralization	**Enzyme Leach** shows multi-point Cu anomaly directly over mineralization Anomaly contrast = 10 **Acetic Acid** shows multi-point zinc anomaly directly over mineralization Anomaly contrast = 10 **0.1N HCl** shows multi-point Ag anomaly directly over mineralization and an unexplained single-sample anomaly 40 m to the north Anomaly contrast = 4 **Hydrofluoric Perchloric** shows no response to mineralization	Smith et al. (1993)
Shoot Gold Zone	120 km northwest of Kirkland Lake	30-40 m thick succession of till, and glaciofluvial, and glaciolacustrine sediments related to 3 advances and one possible readvance	Moderately dipping, auriferous, slightly pyritic quartz veins in sheared altered ultramafics; the zone is 10-15 m wide with a strike length of 200 m and is sub-parallel to the Destor-Porcupine Fault Zone	Very complex anomaly patterns; background for most elements (Cu, Mo, Sn etc.) is higher in clay overburden relative to adjacent esker sands Jackson (1995) notes "rabbit ear" anomalies over the west end mineralization, but these are probably related to surface environmental processes rather than buried mineralization. Anomaly contrast = 2 to 10	Jackson (1995)
Stimson Base Metal Zone	170 km northwest of Kirkland Lake	30-40 m of glaciolacustrine clay with minor boulder till at the base of the sequence	100 m wide by 300 m long, steeply dipping zone (2-3% Zn, 1% Pb, 0.5% Cu) comprised of semi-massive pyrite/ pyrrhotite with lesser disseminated chalcopyrite, sphalerite, and galena hosted by altered felsic tuff and tuff breccia which is overlain by graphitic sediments	Very noisy profiles with insufficient background data; Ti, Zn, and Ga, form "rabbit ear" anomalies that straddle buried mineralization but element levels also increase towards the north end of the line for unknown reasons Cd forms apical anomalies over both mineralized and background areas Anomaly contrast = 2 to 10	Jackson (1995)
Hislop Gold Deposits	60 km northwest of Kirkland Lake	20 m of clay-rich, boulder till	15-20 m wide by 1000 m long zone consisting of three sub-economic deposits (2-10% sulphide) hosted by carbonate breccia in a fault zone that is sub-parallel to the Destor-Porcupine Fault Zone	Single-point Mo, W, and Au anomalies up- and down-ice of mineralization; concentration levels are near detection limit so the anomalies may represent analytical noise Anomaly contrast = 50 (for Au) **Aqua Regia** profile is flat for indicator elements	Jackson (1995)

29

Table 1.5 (continued) Enzyme Leach Case Studies

Property	Location	Overburden	Mineralization	Comments	Reference
PK-Showing	Northern Quebec	0.8 to 2 m of poorly sorted basal till	Massive sulphide in interflow sediments (4.7% Zn/9.8 m)	Multi-point Cu anomaly over mineralization Anomaly contrast = 20	Seneshen (1997)
Clyde River	80 km southwest of Ottawa, Ontario	Less than 4 m of poorly sorted basal till	Narrow sphalerite lenses in dolomite; up to 17% Zn and 850 ppm Cd	Erratic single-point Zn anomalies near mineralization Anomaly contrast = 7	Seneshen (1997)
Dundonald	50 km northeast of Timmins	0-41 m glaciofluvial gravelly sand and local glaciolacustrine silty sand lenses	**Dundeal Zone:** blebby pyrrhotite-pentlandite-chalcopyrite at base of komatiite sequence (1.5-3.04% Ni) **Terminus Zone:** semi-massive pyrrhotie-sphalerite in graphitic interflow argillite (2.5% Zn, 0.5% Cu)	Multi-point Ni, Cu, Zn, Fe, U, V, Y, La, Ce, and Nd anomalies over the Dundeal Zone; no response over Terminus Zone. Anomaly contrast = 3 to 10	Seneshen (1997)
Snake Lake	Northern Manitoba	10 to 20 m of ground moraine till	Sphalerite and chalcopyrite stingers in sheared felsic volcanics	Erratic Cu anomalies near mineralization Anomaly contrast = 3	Seneshen (1997)
Birchtree	Northern Manitoba	5 m of basal till overlain by 25 m of glaciolacustrine clayey silt	Blind Ni mineralization in peridotite boudin (2% Ni/18 m)	Single-point Ni , V, and Br anomalies and depletion of aqua regia extractable Cu, Ni, etc. near mineralization Anomaly contrast = 2 to 3	Seneshen (1997)
Clay Pit Deposit	Getchell Trend, Nevada	Blind gold mineralization covered by 70 m of argillized Tertiary felsic volcanics, which in turn, are overlain by 80 m of alluvium	Fault-controlled, epithermal gold mineralization hosted by Cambrian carbonates and shales	"Rabitt ear" anomalies in As, Sb, Br and other oxidation suite elements that straddle mineralization with a central low directly over mineralization Insufficient background data Anomaly contrast = 8	Clark (1993)
Mansa Mina	Southwest of Chuquicamata in Chile	100 m of alluvial pediment gravels with near surface caliche sheets	Fault-bounded hypogene chalcopyrite mineralization	Single-point Cu, Zn, Cd, Ni, Co, Mn, U, Y, Mo, Pb, Sb, and Y anomalies over and adjacent to mineralization "Rabbit ear Br, I, Re, and Se anomalies straddle mineralization Anomaly contrast = 10 to 175	Seneshen (1997)
Radomiro Tomic	North of Chuquicamata in Chile	0-150 m of alluvial pediment gravels with near surface caliche sheets	Supergene-enriched Cu mineralization, hosted by the Chuquicamata Porphyry In ascending order, the deposit consists of hypogene chalcopyrite veins, super-gene chalcocite and atacamite, and local exotica-type chrysocolla mineralization at the base of the gravels	"Rabbit ear" halogen anomalies (Cl) straddle a post-ore fault running through the centre of the orebody Single-point As and V anomalies over the entire porphyry host Single-point Cu anomalies in areas remote from mineralization are interpreted as "collapsed relic halos" of a former oxidation cell (Clark, 1996) Anomaly contrast = 5 to 20	Clark (1996) Seneshen (1997)

30

Table 1.6 Deionized Water Leach Case Studies

Property	Location	Overburden	Mineralization	Comments	Reference
Dundonald	50 km northeast of Timmins	0-41 m glaciofluvial gravelly sand and local glaciolacustrine silty sand lenses	**Dundeal Zone:** blebby pyrrhotite-pentlandite-chalcopyrite at base of komatiite sequence (1.5-3.04% Ni) **Terminus Zone:** semi-massive pyrrhotite-sphalerite in graphitic interflow argillite (2.5% Zn, 0.5% Cu)	Multi-point Ni, Cu, Zn, U, Fe, H, Ca, Mg, K, Al, Ti, V, Y, La, Ce, Nd, and conductivity anomalies over the Dundeal Zone; no response over Terminus Zone. Anomaly contrast = 3 to 10	Seneshen (1997)
Snake Lake	Northern Manitoba	10 to 20 m of ground moraine till	Sphalerite and chalcopyrite stingers in sheared felsic volcanics	Multi-point Cu anomaly over mineralization H and conductivity anomalies adjacent to mineralization Pb and Ba anomalies related to grain size change in B-horizon soil Anomaly contrast = 3	Seneshen (1997)
Birchtree	Northern Manitoba	5 m of basal till overlain by 25 m of glaciolacustrine clayey silt	Blind Ni mineralization in peridotite boudin (2% Ni/18 m)	Single-point Cu, Zn, Br, I, V, Y, and conductivity anomalies over and adjacent to mineralization Multi-point Ca, Mg, K, and H anomalies over and adjacent to mineralization Anomaly contrast = 2 to 10	Seneshen (1997)
Mansa Mina	Southwest of Chuquicamata in Chile	100 m of alluvial pediment gravels with near surface caliche sheets	Fault-bounded hypogene chalcopyrite mineralization	Single-point Cu, Zn, Cd, Ni, Co, Mn, U, Y, Mo, Pb, Sb, Al, and Y anomalies over and adjacent to mineralization "Rabbit ear Br, I, Re, and Se anomalies straddle mineralization Single-point As, V, K, Na, Mg, Sr, and Ba anomalies over pyritic porphyry host Anomaly contrast = 6 to 400	Seneshen (1997)

31