Adjustment of weak partial extraction data assuming metal ion adsorption: examples using bulk cyanide leach

Andrew W. Rate1,*, Rebecca E. Hamon1,2, Leigh F. Bettenay3 & Robert J. Gilkes1
1School of Earth & Environment, The University of Western Australia, Mail Delivery Point M087, 35 Stirling Highway, Crawley WA 6009, Australia
2Current address: Plant Chemistry Section, Agricultural and Environmental Chemistry Institute, Faculty of Agricultural Sciences, Universita Cattolica del Sacro Cuore, Via Emilia Parmense 84, I-29100, Piacenza, Italy
3Inkanti Pty. Ltd., P.O. Box 1868, Subiaco WA 6008, Australia
*Corresponding author (e-mail: andrew.rate@uwa.edu.au)

ABSTRACT: Geochemical analysis of soils using partial extractions, purported to detect only a fraction of elements mobilized during dispersion, represents a useful exploration tool. Interpretation of partial extraction data is, however, subject to uncertainty because the effects of changing soil or sediment properties on extraction are poorly defined. In particular, soil properties which are known to affect the retention of metal ions (e.g. clay content, organic carbon content, pH) may provide useful parameters against which to calculate adjusted total and partial assay values and thereby enhance anomaly contrast in geochemical exploration. Bulk cyanide leach (BCL), a commonly-used weak partial extraction technique, reduces the nugget effect for Au and can provide higher anomaly contrast than total elemental analyses. For a range of elements (Ag, Au, Cd, Co, Cu, Mo, Ni, Pd and Zn), we conducted BCL determinations, measured the same elements by NAA, XRF or aqua regia digest, and determined a range of soil chemical properties for traverses at 10 exploration prospects in Australia and Namibia. Raw total and BCL data were compared with (i) concentration : soil parameter ratios, and (ii) adjusted BCL values based on a simple model of trace element speciation in soils. Anomaly contrasts for raw and normalized or adjusted data were compared using an estimate of anomalism based on both quantitative and heuristic criteria. At prospects with soils containing detectable carbonate, normalization of total and BCL assays to carbonate content significantly improved multi-element anomaly contrast. Normalization to amorphous Fe or Mn oxide content, or total Al, K or Mg also significantly improved anomaly contrast at fewer prospects. Adjusting BCL values using a simple adsorption model also showed limited success in improving anomaly contrast, and represents a useful framework for interpreting weak partial extraction data.

KEYWORDS: geochemical exploration, trace elements, precious metals, base metals, bulk cyanide leach

SUPPLEMENTARY MATERIAL: Data tables relating to study are available at http://www.geolsoc.org.uk/SUP18409.
other elements. Other techniques for partial extraction of metals in soils are known to be affected by basic soil properties such as pH, texture, and soluble salt content. For example, high soil pH may increase retention of metal cations by adsorptive phases, or precipitation as insoluble minerals (McBride 1989), thus rendering them less available to weak extracting solutions such as 0.25% NaCN.

Anomalous concentrations of metals in soils may reflect underlying mineralization, but may also correspond to spatial variability in the soil's ability to retain metal ions. We worked on an initial assumption that anomaly contrast may improve if 'total' metal concentrations are normalized against soil property parameters (i.e. elemental measurements divided by soil property parameter), where a soil anomaly is masked by spatial variation in one or more bulk soil properties that favour metal retention (e.g. iron oxide or total Fe content; Hamon et al. 2004). Such an approach approximates the calculation of residuals to identify anomaly contrast. Although the extractable amount of an element is not identical to its aqueous activity, we can approximate 'extractability' of an element by a partial extractant by the ratio (M/SM). Rearranging Equation 2 to solve for this ratio gives:

\[
\frac{M}{SM} = \frac{H}{K(\equiv SH)}
\]  

We can further assume that (\equiv SH) approximates the concentration of the adsorbing phase such as organic carbon, clay or oxide mineral in a soil (strictly, (\equiv SH)+(\equiv SM), which \approx (\equiv SH) at low surface coverage). Since extractability decreases as both pH and concentration of adsorbent increase, an adjusted extractable-element value can be obtained by multiplication of partial extraction concentrations by the reciprocal of extractability (i.e. (\equiv SH) / (H); from Equation 3, treating \( K \) as a simple proportionality factor). This adjusted concentration should minimize any changes in extractability of elements across a landscape due to changes in soil properties (i.e. extractability) and more closely represent potentially anomalous variations.

Our aims were therefore to: (i) measure total elemental concentrations, BCL-extractable metal concentrations, and a

Table 1. Site and soil descriptions.

| Prospect          | Description*                                                                 |
|-------------------|-------------------------------------------------------------------------------|
| Claypan           | The Claypan prospect is in the northeastern region of Western Australia's Yilgarn Block. This area is characterized by indurated, proximal latelite derritus and aeolian sands, with no observable calcrete, overlying variably stripped and often intensively leached Archaean bedrock sequences. Zones of hardpan development, with some Mn enrichment, are common. The upper saprolite is overlain by 10–12 m of transported colluvium. The land surface is dissected by major tertiary palaeochannels that have little or no surface expression. A sharp, low intensity, MMI Au anomaly directly overlies weak bedrock Au mineralization in a complex shear zone associated with porphyries in a complex ultramafic/mafic/sedimentary system. |
| Ryansville        | The Ryansville prospect in the Murchison Province, Yilgarn Block, Western Australia is characterized by acidic gravelly surface soils with a sandy matrix, sampled at the base of colluvium/talus on the northern slope of the Weld Range. Initial BCL analyses showed Ag and Cu anomalism down slope of known mineralization. Colluvium is derived from a banded iron formation/mafic complex on the ridge crest. |
| Ombombo           | The Ombombo prospect in Namibia is underlain geologically by Proterozoic platform sediments, dominated by carbonates and arkosic sandstones. The regolith is characterized by shallow profiles with abundant surficial carbonates. Soil sampling was conducted along strike of outcropping minor copper mineralization in and around surface soils of aeolian origin. |
| Gala              | The Gala prospect, south of Kalgoorlie, Western Australia, contains predominantly red loamy calcareous soils developed on proximal colluvium from mafic and ultramafic bedrock. An alluvial channel crosses the prospect. |
| Blue Haze, Crossroads, West Quest | The Blue Haze, Crossroads and West Quest prospects are south of Southern Cross, Western Australia. Calcareous soils with moderate clay contents at depth are covered with a thin layer of sandy/silty (possibly aeolian) material. Soil samples are from >30 cm depth. |
| Bugeye, Silverstone | Bugeye and Silverstone are gold prospects are located in the Minjar Range area of Murchison Province near the Golden Grove Cu-Zn-Pb-Au deposit, 240 km east of Geraldton, Western Australia. Mineralized bedrock at Bugeye is overlain by a thin (1–2 m maximum) layer of indurated distal colluvium, with no signature of underlying mineralization in the surface soil (Bolster 1994a). The Silverstone prospect is on alluvium within a broad shallow alluvial system up to 15 m in thickness overlying mineralized bedrock (Bolster 1994b); some Silverstone soils contain pedogenic carbonate. Surface soil sampling at Silverstone showed anomalous elemental analyses for Au which closely reflect the surface projection of underlying mineralization. The soil samples were collected from transported overburden that lies above a pisolitic laterite unit, overlying the molttled and pallid zones of the weathering profile. |
| Reynolds Range    | The Reynolds Range prospect in the Northern Territory, Australia, is characterized by red-brown soils with sandy or sandy loam texture, with an alluvial channel dissecting the prospect. |
Table 2. Anomalism in raw BCL assays for each traverse fulfilling Criteria 1 and/or 2 (Criterion 1: highest assay vertically over, or within 1 field sampling point of, known mineralization; Criterion 2: the standardized residual value or z-score of an anomalous point is >2).

| Transect       | Elements for which ‘Criterion 1’ anomalism occurred (in order of decreasing z-score) | Elements for which both Criteria 1 and 2 anomalism occurred (in order of decreasing z-score) |
|----------------|--------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Claypan        | Co > Cd > Ag > Ni > Pd > Zn                                                          | –                                                                                         |
| Ryansville     | Au                                                                                    | –                                                                                         |
| Omnhombo       | Co > Cd > Ni > Ca > Ag                                                              | Co                                                                                        |
| Gala 18600N    | Ni > Pd > Au > Ag > Zn*                                                             | –                                                                                         |
| Gala 18600N    | Co                                                                                    | –                                                                                         |
| Blue Haze      | Cd = Zn > Mo > Au > Ag                                                              | Cd = Zn                                                                                   |
| West Quest     | Au* > Mo > Co > Zn > Ag > Cu > Ni                                                   | Au*                                                                                       |
| Crossroads     | Mo > Zn > Ni > Au                                                                  | –                                                                                         |
| Bugeye 6400N   | Pd > Co > Ag                                                                        | –                                                                                         |
| Bugeye 6450N   | Mo > Au > Pd > Ag > Cu > Co                                                          | –                                                                                         |
| Silverstone 16400N | Mo > Au > Cd > Ni > Ag > Cu > Pd                                                   | Mo                                                                                        |
| Silverstone 16500N | Mo > Ca > Ni > Cd > Pd > Ag > Cu > Co                                               | –                                                                                         |
| Reynolds Range SE | Cd > Cu > Mo > Ni                                                                  | –                                                                                         |
| Reynolds Range NW | –                                                                                   | –                                                                                         |

* highest concentration at terminal point of traverse, so may not represent peak value.

range of basic properties, for soils from a range of highly weathered environments, and (ii) quantitatively compare anomaly contrast across exploration transects for raw, and normalized or adjusted, total and BCL assay data.

MATERIALS AND METHODS

Soil preparation

The soils used in this project were archived samples from traverses across mineralization at 10 prospects in Australia, and one prospect in Namibia, representing different regolith environments (Table 1). Summaries of basic chemical and mineralogical properties of soils from each prospect are given in Tables 1 and 2 of Supplementary material, and trace element concentrations appear in Table 3 of Supplementary material.

Individual soil samples were selected on the basis that they appeared to have anomalous Au, plus samples directly adjacent in the transects to these samples that did not have anomalous Au concentrations, providing there was sufficient soil available. Soil was gently crushed to break soil aggregates, sieved to ~2 mm through plastic mesh, and 100 g stored for analyses in a plastic container. All analyses, except pH, EC, NAA and BCL, were carried out using these 100 g sub-samples.

Soil analysis

Cyanide leach extractions of soil were performed by Assay Research Ltd., Perth, Western Australia. A bulk sub-sample of the ~2 mm fraction of soil (400–500 g) was shaken with 1.08 l of 0.25% NaCN solution following the addition of 1–2 g Ca(OH)2. Supernatant solutions were diluted as appropriate and Au, Ag, Pd, Cd, Cu, Ni, Zn, Co and Mo were determined by graphite furnace atomic absorption spectrometry (GFAAS).

In preparation for total elemental analyses by X-ray fluorescence spectrometry (XRF), 10 g of the 2 mm-sieved fraction of soil was pulverized in a Sylan (silicon nitride) bowl. Duplicate samples were diluted and thoroughly mixed with binding agent (Hoechst wax) in a ratio of 8:2.5 (soil:wax), then pressed into pellets (7 tonnes for 30 seconds) and stored in sealed plastic bags until analysis. Pellets were analysed using a Philips PW1400 instrument fitted with a Rh tube. Synthetic standards (element oxides mixed in pure SiO2) were used to calibrate for As, Pb, Ni, Co, Cu, Mo, Ba, Sr, Ti, Zn, Cr, V, Y and Zr. Certified reference materials were used for calibration of Al, Ca, Fe, K, Mg, Mn, P, S, and Si as well as for corrections for inter-element and matrix effects. Minimal spectrometer drift was confirmed by regular measurement of an external monitor sample (Karathanasis & Hajek 1996).

Total and organic carbon contents were measured for each sample using a Leco CHN-1000 Analyzer. Samples were ground as for XRF and then oven-dried at 105°C to remove residual water. EDTA standards were used to calibrate for carbon. To remove carbonate prior to determination of organic carbon, samples were pretreated with 6 M HCl (Nelson & Sommers 1996). Carbonate-C was determined by difference between total carbon and organic carbon; no assumptions were made about the carbonate mineral(s) present.

Measurement of specific surface area (m²/g) was carried out on oven-dry samples using nitrogen adsorption at five different relative pressures (BET multi-point analysis) using a Micromeritics Gemini III 2375 Surface Area Analyser. Quality control was maintained using a reference kaolin standard, which was re-analysed at regular intervals between samples. Duplicates and replicates were analysed to gauge the reproducibility of the method. Duplicates (machine) error for surface area was in the order of ±2% for most samples, with duplicate (sub-sampling) error c. ±5%.

Oxalate-extractable Fe and Mn were determined using the method described by Loeppert & Inskeep (1996). Soil pH was measured in 1:2.5 soil:water extracts using a combined pH/reference electrode coupled to an Orion EA-940 pH/mV meter.

Numerical analyses

Raw total (i.e. values used to derive Table 3 of Supplementary material) and BCL assays of Au, Ag, Pd, Cd, Co, Cu, Mn, Mo, Ni and Zn were compared graphically with the corresponding values following normalization to the following parameters: total Al, Ca, K, Fe, Mg, Mn, and Si; organic C; CO3-C (if present); specific surface area; and oxalate-extractable Fe and Mn. In addition, adjustment factors designed to counter the effect of varying extractability were applied to BCL assay data: (i) % Organic C / [H⁺]; (ii) oxalate Fe / [H⁺]; (iii) XRF Al / [H⁺]. Organic C and oxalate Fe were selected to represent distinct adsorbing phases, while total (XRF) Al approximates clay content for highly weathered soils (cf. Purdie et al. 1992 – we did not determine clay content directly for all soil samples). We assumed that our measured soil pH values could provide an adequate estimate of [H⁺] = 10− pHT.
Anomalism was defined as fulfilling these two criteria: (1) highest raw BCL or normalized value vertically over, or within one field sampling point of, known mineralization; (2) the standardized residual value or z-score (compared with the mean value for a transect) of an anomalous point was 2.0 or higher (Howarth 1984; Yusta et al. 1998). Standardized residuals are defined in Equation 4:

\[ z_i = \frac{x_i - \bar{x}}{s} \quad (4) \]

where \( z_i \) is the standardized residual for the \( i \)th datum in a transect, \( x_i \) is the \( i \)th datum, \( \bar{x} \) is the mean value for the transect and \( s \) is the sample standard deviation for the transect (Laws Agricultural Trust 1997).

**RESULTS**

According to both Criteria 1 and 2 above, total elemental concentrations were anomalous at only two prospects (Table 4 of Supplementary material): Ombombo (Cu) and Crossroads (Ni). Raw BCL analyses gave anomalous concentrations, defined by both criteria, in more instances than total analyses. BCL anomalies for Au, defined by both criteria above, were present at Ryansville and West Quest. Anomalies were also observed in raw BCL data for Cd and Zn from Blue Haze, Co at Ombombo, and Mo at Silverstone. No BCL anomalism was apparent for the elements Ag, Pd, Ni, or Cu, or at the prospects Claypan, Gala, Crossroads, Bugeye or Reynolds Range, if the apparent for the elements Ag, Pd, Ni, or Cu, or at the prospects Ombombo, and Mo at Silverstone. No BCL anomalism was observed in raw BCL data for Cd and Zn from Blue Haze, Co present at Ryansville and West Quest. Anomalies were also defined by both criteria, in more instances than total analyses.

| Transect            | Raw BCL | Organic C (%) | Carbonate C (%) | Specific surface area | Oxalate Fe | Oxalate Mn | Soil pH | Soil EC |
|---------------------|---------|---------------|-----------------|-----------------------|------------|------------|---------|---------|
| Claypan             | –       | –             | na†             | –                     | –          | –          | –       | –       |
| Ryansville          | Au†     | –             | na†             | Au†                   | –          | –          | –       | –       |
| Ombombo             | Co†     | –             | na†             | Co> Ni> Cd            | Co> Cd> Au> Ni> Cd | Ni> Co> Co | –       | –       |
| Gala 18400N         | Co      | –             | Co> Cd> Ni> Zn  | Mo> Au                | Co> Pd> Co | Co> Cd> Pd | –       | –       |
| Gala 18600N         | Co      | –             | Co> Cd> Ni> Zn  | Mo> Au                | Co> Pd> Co | Co> Cd> Pd | –       | –       |
| Blue Haze           | Cd=Zn   | Au Ni> Cd> Cd| > Ag> Cu> Pd    | Mo> Au                | Mo> Cd> Co | –          | Au      | Mo> Zn |
| West Quest          | Au*     | Au Ni> Cd> Cd| > Ag> Cu> Pd    | Mo> Au                | Mo> Cd> Co | –          | Au*     | –       |
| Crossroads          | – Mo    | –             | Na†             | –                     | –          | –          | –       | –       |
| Bugeye 6400N        | –       | –             | na†             | –                     | –          | –          | –       | –       |
| Bugeye 6450N        | –       | –             | na†             | –                     | –          | –          | –       | –       |
| Silverstone 16400N  | Mo      | Cd            | –               | –                     | Mo         | –          | Cd      | –       |
| Silverstone 16500N  | – Pd    | –             | –               | –                     | –          | –          | –       | –       |
| Reynolds Range SE   | –       | –             | Na†             | –                     | –          | –          | –       | –       |
| Reynolds Range NW   | –       | –             | Na†             | –                     | –          | –          | –       | –       |

* highest concentration at terminal point of traverse, so may not represent peak value.
† No carbonate detected in soil.

Even considering a range of possible adsorbents, adjustment of BCL data using factors that assumed that variability in extractability was controlled by simple pH-dependent adsorption (Equation 3 above) also improved anomaly contrast in some cases. Improvements in contrast for adjusted BCL data were occasionally spectacular (e.g. Fig. 3) but anomalism fulfilling both criteria was observed at only four prospects (Table 4).

**DISCUSSION**

The use of [H+] instead of pH to adjust BCL values produces data that have skewed distributions, due to the large
relative differences in $[H^+]$. Unless it can be shown that anomalous values do represent a separate population, adjusted data should strictly be transformed to remove skewness. Some preliminary investigation using log10-transforms showed that this suppressed anomalism defined by both Criteria 1 and 2, producing a narrower data range with low \( z \)-scores. This approach clearly requires further investigation using more extensive datasets.

Normalization of total trace element data to soil properties or major element concentrations will only improve anomaly contrast when the normalizing property represents a trace element sink, or increases trace element immobilization. Similarly, normalization of BCL analyses to soil properties or major element concentrations will only be successful in improving anomaly contrast in situations where the normalizing property increases BCL extractability. There is some evidence that carbonate minerals in soils and regolith may provide a sink for Au (Lintern & Butt 1993), and therefore there may be a positive correlation of total Au and carbonate content. The findings presented in this paper suggest that the Au in soils containing carbonate is easily extracted by BCL, and therefore normalization of BCL Au values to soil carbonate content increases anomaly contrast. It is interesting that these relationships appear to extend to several other elements (Ag, Pd, Cd, Co, Ni, Cu, Zn, Mo). Adsorption on or inclusion into carbonates has been demonstrated for several elements (Han & Banin 1996; Lintern & Butt 1997). An increase in anomaly contrast would, however, also be expected if there was depletion of soil carbonate over buried mineralization, and for some traverses this is the case (e.g. at maximum Au and/or Co/Cu/Ni/Zn, Gala 18600N: \( z \)-score for $CO_3^2$-C = -1.34; West Quest: \( z \)-score
For CO$_3$-C = -1.12). For the Crossroads prospect there is no such depletion of CO$_3$-C, and no improvement in anomaly contrast is observed following normalization of BCL (Figs 1 and 2) or total concentrations to soil carbonate content. The mechanism by which carbonate might be depleted in soil and regolith above mineralization may reflect sulphide weathering and subsequent acidification and dissolution of carbonate (Hamilton et al. 2004), or inhibition of carbonate precipitation in soils already acidified by sulphide oxidation. It should also be noted that normalization to total Ca (Tables 5 and 7 of Supplementary material) did not provide the same improvements in anomaly contrast as did normalization to CO$_3$-C (Table 6 of Supplementary material; Table 3). Calcium content cannot, therefore, be used as a proxy for carbonate content in this suite of soils, despite the weak but significant correlation between Ca and CO$_3$-C. This may reflect the existence of Ca in other mineral phases, such as feldspars (Table 1 of Supplementary material), or the presence of carbonates other than calcium.
carbonate (soil Mg contents were similar to soil Ca contents; Table 2 of Supplementary material).

The improvement in anomaly contrast, in some instances, when raw BCL data are normalized against specific surface area, XRF Al or XRF K may represent the correlation of all of these parameters with soil clay content, and a reduction in the extraction efficiency of BCL with increasing soil clay content. Total Al has been used as a proxy for clay content of soils and sediments (Pardue et al. 1992; Rose et al. 1979). A positive correlation between XRF Al and clay content ($r^2 = 0.503; p<0.001$), and specific surface area and clay content ($r^2 = 0.491; p<0.001$), exists for these soils; such a correlation does not exist between XRF K and clay content ($r^2 = 0.006; p=0.66$).

The lack of obvious improvement in anomaly contrast when total data are normalized to organic carbon content and soil pH is surprising, given the well-established influence of these soil properties on metal speciation (McBride 1989). Organic carbon may also affect BCL extractability by scavenging metal-cyanide complexes from the leach solution (pers. comm., 1999, W. Griffin; cf. Hiller & Brümmer 1997; Marsden & House 1992). The initial pH of a soil might be expected to affect cyanide extractability by controlling the final pH of the BCL system (especially if the soil is well-buffered and pH is adjusted by a constant addition of lime), since cyanide speciation is very pH-dependent (Wang & Forssberg 1990). Similarly, it was expected that reactive iron and manganese oxide content (estimated from oxalate-extractable Fe and Mn) would have improved anomaly contrast for more traverses, since both such phases are known to be significant adsorptive phases for metals in soils (Cornell & Schwertmann 1996; McKenzie 1980). The general lack of improvement in anomaly contrast when BCL data are normalized against these parameters may indicate that cyanide is able to solubilize all or most of the adsorbed metal ions in soils, without dissolving the adsorptive phases themselves and releasing structural metal ions. Normalizations of total elemental data against the same soil properties, however, gave even fewer improvements in anomaly contrast than for BCL, suggesting that incomplete extraction by BCL was not the issue. It is more probable that a single soil property will not account for all the non-anomalous variability in total concentrations or BCL extractability. In this case a more integrative parameter, such as total Al or specific surface area which may correlate with the adsorptive capacity of the whole soil, is more likely to improve anomaly contrast.

**Fig. 6.** Cobalt anomalism (raw BCL (♦) and BCL/oxalate Mn ratio (△)) for the Gala traverse at 18600N; peak $\zeta$-score $= 2.05$ for raw BCL and 2.13 for BCL/oxalate Mn ratio. Shaded area shows buried mineralization.

**Table 4.** Anomalism in raw BCL and adjusted BCL assays for each traverse fulfilling both Criteria 1 and 2 (Criterion 1: highest concentration vertically over, or within 1 horizontal point of known mineralization; Criterion 2: the standardized residual value or $\zeta$-score of an anomalous point is $>2$).
CONCLUSIONS

This work presents a simple and rational method for transforming weak partial extraction data for geochemical exploration in soils, using accessory data to limit the confounding effects of soil property changes. The data transformation method is based on the assumption that extractability is controlled by adsorption, which was able to improve anomaly contrast for some elements at some prospects but, with any method, it was not universally applicable. Since the method is based on a credible understanding of how metal ions behave in regolith environments, it is worth pursuing further for weak partial extractions other than bulk cyanide leach and in a range of regolith environments.

Normalization of total and BCL elemental concentrations to soil carbonate content significantly improves anomaly contrast for 2–9 elements, in soils containing detectable carbonate. In addition, normalization of total or BCL data to amorphous Fe or Mn oxide content in soil also significantly improved anomaly contrast at two prospects, as did normalization to total Al, K or Mg at further two prospects. The simple normalization technique therefore offers a quantitative improvement in geochemical anomaly detection, particularly in soils containing detectable carbonate. In soils, using accessory data to limit the confounding effects of soil property changes, this work presents a simple and rational method for transforming weak partial extraction data for geochemical exploration in soils, using accessory data to limit the confounding effects of soil property changes. The data transformation method is based on the assumption that extractability is controlled by adsorption, which was able to improve anomaly contrast for some elements at some prospects but, with any method, it was not universally applicable. Since the method is based on a credible understanding of how metal ions behave in regolith environments, it is worth pursuing further for weak partial extractions other than bulk cyanide leach and in a range of regolith environments.

Normalization of total and BCL elemental concentrations to soil carbonate content significantly improves anomaly contrast for 2–9 elements, in soils containing detectable carbonate. In addition, normalization of total or BCL data to amorphous Fe or Mn oxide content in soil also significantly improved anomaly contrast at two prospects, as did normalization to total Al, K or Mg at further two prospects. The simple normalization technique therefore offers a quantitative improvement in geochemical anomaly detection, particularly in soils containing detectable carbonate. Further research could be directed towards establishing whether other soil components as normalizing parameters work best when that component is abundant in soil (as is the case for carbonate-C). Other profitable avenues for development of new approaches for manipulating data from weak partial extractions may be generated using two general assumptions. First, when a soil component retains a target element in a form that is extracted by a partial leach, then normalization with respect to that parameter should improve anomaly contrast. Second, when a soil component retains a target element in a form that is not extracted by a partial extractant, then a transformation based on pH-dependent adsorption (probably on the most favourable or most abundant adsorbent), may increase anomaly contrast. If these assumptions are valid, there may be considerable benefit to collecting, more widely, accessory soil or sediment data in exploration programs.

The authors acknowledge the financial support of the Australian Research Council, M.I.M. Exploration Pty. Ltd, and Normandy Exploration Ltd.

REFERENCES

Birrell, R. 1992. Ongoing development and application of bulk leach technology in exploration. *Explor.,* 74, 11–13.

Chau, T.T. 1984. Use of partial dissolution techniques in geochemical exploration. *Journal of Geochemical Exploration,* 20, 101–135.

Cornell, R.M. & Schwertmann, U. 1996. *The Iron Oxide: Structure, Properties, Reactions, Occurrence and Uses.* VCH Verlagsgesellschaft, Weinheim.

Felipek, L.H. & Theobald, P.K.J. 1981. Sequential extraction techniques applied to a porphyry copper deposit in the Basin and Range Province. *Journal of Geochemical Exploration,* 14, 155–174.

Fletcher, K. & Horsley, S. 1988. Determination of gold by cyanidation and graphite furnace atomic absorption spectroscopy. *Journal of Geochemical Exploration,* 30, 29–34.

Hamilton, S.M. 1998. Electrochemical mass-transport in overburden: a new model to account for the formation of selective leach geochemical anomalies in glacial terrain. *Journal of Geochemical Exploration,* 63, 155–172.

Hamilton, S.M., Cameron, E.M., McClanaghan, M.B. & Hall, G.E.M. 2004. Redox, pH and SP variation over mineralization in thick glacial overburden; Part II, Field investigation at Cross Lake VMS property. *Geochemistry: Exploration, Environment, Analysis,* 4, 45–58.

Hamon, R.E., McLaughlin, M.J., Gilets, R.J., Raye, A.W., Zarcinas, B., Robertson, A., Cozens, G., Radford, N. & Bettany, L. 2004. Geochemical indices allow estimation of heavy metal background concentrations in soils. *Global Biogeochemical Cycles,* 18, doi:10.1029/2003GB002063.

Han, P. & Bann, A. 1996. Solid-phase manganese fractionation changes in saturated arid-zone soils; pathways and kinetics. *Soil Science Society of America Journal,* 60, 1072–1080.

Hiller, D. & Brunner, G. 1997. Microprobe studies on soil samples with varying heavy metal contamination. 2. Contents of heavy metals and other elements in aggregations of humic substances, litter residues and charcoal particles. *Zeitschrift für Pflanzenernährung und Bodenkunde,* 160, 47–55.

Hoffman, S.J. 1987. Soil sampling. In: Robertson, J.M. (ed.) *Exploration Geochemistry: Design and Interpretation of Soil Surveys.* Society of Economic Geologists, Chelsea, MI, 39–77.

Howard, R.J. 1984. Statistical applications in geochemical prospecting: A survey of recent developments. *Journal of Geochemical Exploration,* 21, 41–61.

Karakhanian, A.D. & Hajek, B.F. 1996. Elemental analysis by X-ray fluorescence spectroscopy. In: Sparks, D.L. et al. (eds) *Methods of Soil Analysis. Part 3 – Chemical Methods.* SSSA Book Series, Soil Science Society of America, Madison, WI, 161–223.

Laws Agricultural Trust 1997. *Genius 5 Recharts 4.1 (PC/Windows NT).* Oxford University Press, Oxford.

Lintern, M. & Butter, C. 1993. Pedogenic carbonate: an important sampling medium for gold exploration in semi-arid areas. *Exploration Research News,* 7, 7–11.

Linton, M. & Butter, C.R.M. 1997. Gold exploration using pedogenic carbonate (calcrete). In: Eggleyton, R.A. (ed.) *The State Of The Regolith: Proceedings of the Second Australian Conference on Landscape Evolution and Mineral Exploration.* Geological Society of Australia, Inc., Brisbane, Queensland, Australia, 200–208.

Loopept, R.H. & Inskee, W.H. 1996. *Iron.* In: Sparks, D.L. et al. (eds) *Methods of Soil Analysis. Part 3 – Chemical Methods.* SSSA Book Series, Soil Science Society of America, Madison, WI, 639–664.

Marsden, J. & House, J. 1992. *The Chemistry of Gold Extraction.* Ellis Horwood, New York.

McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils. *Advances in Soil Science,* 10, 1–56.

McBride, M.B., Saté, S. & Hendriksen, W. 1997. Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science,* 48, 337–346.

McKenzrie, R.M. 1980. The adsorption of lead and other heavy metals on oxides of manganese and iron. *Australian Journal of Soil Research,* 18, 61–73.

Nelson, D.W. & Sommers, L.E. 1996. Total carbon, organic carbon, and organic matter. In: Sparks, D.L. et al. (eds) *Methods of Soil Analysis. Part 3 – Chemical Methods.* SSSA Book Series, Soil Science Society of America, Madison, WI, 961–1010.

Parlour, J.H., Delaune, R.D. & Patrock, W.H., Jr. 1992. Metal to aluminum correlation in Louisiana coastal wetlands: identification of elevated metal concentrations. *Journal of Environmental Quality,* 21, 539–545.

Radford, N.W. 1996. BLEG sampling in gold exploration: an Australian view. *Explor.,* 92, 8–10.

Rose, A., Hawkes, H.E. & Weare, J.S. 1979. *Geochemistry in Mineral Exploration.* Academic Press, London.

Sree, B.W. 1998. A new theory to explain the formation of soil geochemical responses over deeply covered gold mineralization in arid environments. *Journal of Geochemical Exploration,* 61, 149–172.

Wang, X. & Forsberg, K.S. 1990. The chemistry of cyanide-metal complexes in relation to hydrometallurgical processes of precious metals. *Mineral Processing and Extractive Metallurgy Review,* 6, 81–125.

Yusta, I., Velasco, F. & Herrera, J.-M. 1998. Anomaly threshold estimation and data normalization using EDA statistics; application to lithogeochemical exploration in Lower Cretaceous Zn-Pb carbonate-hosted deposits, northern Spain. *Applied Geochemistry,* 13, 421–439.

Received 12 December 2007; revised typescript accepted 10 December 2008.