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Some Comments on the Use of Selective Extractions in Geochemical Exploration in Arid Terrains.

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INTRODUCTION

The prevailing wisdom in exploration geochemistry is that the focus of exploration will be increasingly directed towards deposits that display very subtle surface geochemical expression. Such wisdom extends to arid and deeply weathered terrains, such as those encountered in many parts of Australia, where both long periods of leaching of the regolith and the influx of transported surface materials have resulted in either minor or undetectable differences in the total metal content of mineralised and unmineralised areas. There is evidence, however, that even in areas with deep weathering there is vertical transport of trace elements derived from mineralisation and recycling of such elements in the upper sections of the regolith. Processes involved may include groundwater movement, capillary action, diffusion of volatile compounds, natural electrochemical gradients, vegetation recycling and the action of organisms. The net result is that weak geochemical dispersion haloes are actively forming in the top few metres of overburden.

Metals transported by these mechanisms might be expected to occur as transient adsorbed or exchangeable species on existing mineral phases within the overburden, as well as in association with recently developed (and commonly metastable) secondary minerals such as amorphous Fe and Mn oxyhydroxides and carbonates. In most instances, such element accumulations would only represent a small fraction of the total trace element content and, hence, geochemical contrast would be suppressed if total metal extractions were used. In an attempt, therefore, to isolate geochemical signatures related to recent geochemical dispersion, a wide variety of selective geochemical extractions have been used. These have included "traditional" selective extraction techniques and some of the newer generation of methods.

In comparing the results of studies from a range of geochemical terrains (Yeager *et al.*, 1998; Jackson, 1995, Gray *et al.*, 1998; Cohen *et al.*, 1998) it would appear that selective extraction have met with more limited success in deeply weathered and arid terrains than in other terrains, such as the recently glaciated areas of the northern hemisphere. Whether this perception is correct will only be resolved with analysis of a larger compilation of case studies than presently exist in the literature. Case studies in glaciated terrains or deep pediment cover have certainly indicated that both traditional and new generation selective extraction methods (when applied to a range of sampling media) can produce responses that are difficult to directly relate to underlying geology and the location of mineralisation (Bajc, 1998; Smee, 1998).

TERMINOLOGY

A literature survey indicates the interchangeable use of the terms *partial* and *selective* extractions, as indicated in the table below. The term selective does appear to be the more common one used. Confusion of these terms is undesirable as they should connote different processes.

Partial

Clark 1993
Belzile *et al.*, 1989
Malo, 1977
Filipek *et al.*, 1982

Selective

Hall *et al.*, 1996
Yong *et al.*, 1993
Chao and Zhou, 1983
Kheboian and Bauer, 1987
Robinson, 1984
Trolard *et al.* (1995)
Borggaard (1981 *et seq.*)

The concise OED defines these terms as:

Partial 1. *a.* forming only a part, not complete (*a partial success*).
2. *a.* biased, unfair.

Selective 1. *a.* characterised by selection.
2. *a.* using selection.

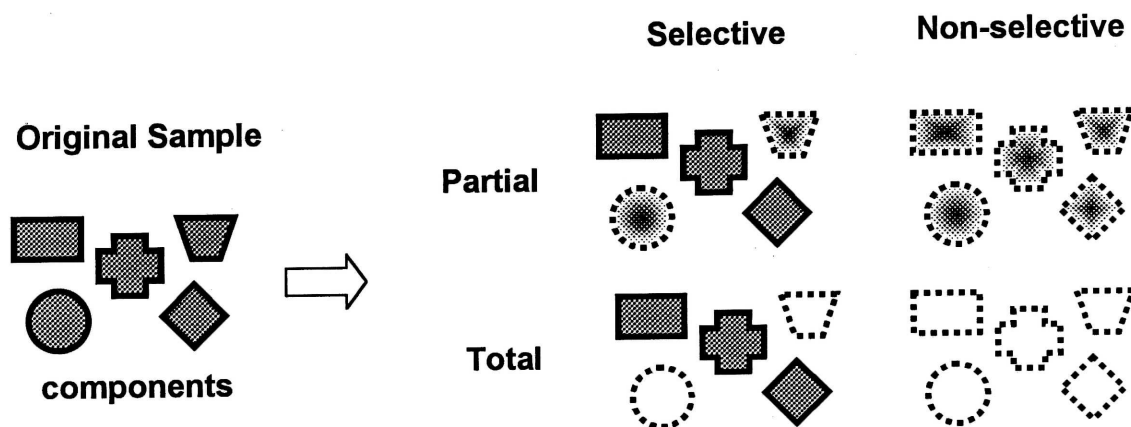
There is a benefit to maintaining separation between these terms, with the following definitions:

Selectivity the ability of a leach to attack specific mineral phases and leave remaining phases unaffected) should be differentiated from the term

Partiality the proportion of the total concentration of an element, associated with the mineral phase(s) targeted, actually released.

The potential exists for “partial selective” extractions to yield greater geochemical contrast between mineralized and background samples than either “partial non-selective” or “total selective” extractions.

A further question of terminology is whether the terms selective or partial should be applied to the mineral components undergoing attack or the elements being released.



SAMPLING PROCEDURES

Site Documentation

Care must also be taken in recognising the wide variation in the natural environment on a sample-by-sample basis. This is particularly so in complex geomorphic terrains where soil type, Eh and pH may vary significantly over short distances in regolith. Many of the problems interpreting selective extraction data relate to poor field documentation and sample site knowledge. This is true for all geochemical sampling and not just for selective leach data, but the problems appear exaggerated for selective leach data. A wider range of geomorphic attributes probably needs to be noted than is the case for surveys that involve total analysis. Examples include the type and density of vegetation cover, drainage/slope direction, geomorphic domain, quartz vein abundance, rock out crop or float lithology, abundance of Fe-lag or pisolites, soil type, sample depth, soil colour, notes on possible contamination etc. All these things are best logged digitally in the field. It is not acceptable to delegate sample collection and site descriptions to field hands.

Sampling Arrays

There is some debate as to whether selective extraction surveys are most effective when conducted on grids or traverses. The choice of options is partly dependent on the size and shape of geochemical dispersion haloes which, in turn, are dependent on factors such as source geometry and element dispersion mechanisms. Most orientation surveys are conducted at close station-spacings along traverse lines normal to the geological fabric of an area. This permits preparation of line profiles that enables recognition of subtle changes in multi-element geochemistry and its relationship to landform and regolith types. Decreasing along-line sample spacing is most likely to result in detection of subtle "short wave length" anomalism associated with buried mineralisation or a mineralised halo developed within joints, fractures or faults, (consider by analogy the better resolution achieved by taking more closely spaced magnetometer readings in a magnetometer survey).

Compositing

Where anomalies tend to be high contrast and backgrounds relatively stable, compositing of sampling may be used. Compositing delivers the advantage of a lower analytical cost without a reduction in the number of sampling sites, however, it also reduces geochemical contrast, especially where few individual samples intersect the anomalous zone. In a soil and vegetation traverse over Au mineralisation at McKinnons (Cobar, NSW) compositing would result in a more narrow anomaly in all three media, but the gain of an anomaly for Enzyme Leach as a function of the high contrast anomalies at a couple of sites (Fig. 1). The laboratory should do the compositing at assay time. This allows for a more representative split of the samples to form the assay composite and also preserves the individual samples for follow-up by assay of the individual site samples.

Where major shifts in geochemical threshold occur, it is important not to mix composite samples from different regolith domains. For example, compositing of samples from alluvial and residual domains should be avoided in the Cobar region due major differences in background population characteristics. Splitting of data into geological, geomorphic and regolith sub-populations may be expedited using, for example, SQL queries in MapInfo. It should be noted, however, that the geomorphic domains themselves span areas where there may be complex geology, structural deformation, or include other features that do not give rise to a uniform geochemical environment. Some reference to idealised conceptual geochemical and terrain models, such as those of Butt and Smith (1980) and Butt and Zeegers (1992), would be of benefit in developing approaches to the interpretation of data.

Sampling Media

In selecting sampling media in arid terrains, the nature of the soil profile needs to be assessed. The upper 10cm or so of a soil profile is typically dominated by "loose" soil that is subject to intense biological activity, is relatively rich in organic materials and may be subject to sheetwash erosion, winnowing and flushing by rainwater and may be of mixed origin. Beneath this and to the top of the C-horizon there is often a well-bound, weakly cemented (by silts, clays, incipient calcrete or ferricrete) B-horizon soil that is an appropriate sampling media for many partial leach methods. Sampling needs to be undertaken at a depth of at least 20-50 cm to ensure that the sample was collected from below the base of the material affected by sheetwash erosion or flushing.

It needs to be remembered that the target for sampling is a longer term or older fixed substrate that has had time to accumulate sufficient precipitates from evaporated ground water (or from other transport mechanisms). The best indication of the appropriate horizon is the presence of Fe-oxide or Mn-oxide spotting or nodule formation in the soil. The enrichment of secondary Fe- or Mn-oxide is often the only visual indicator of the zone of precipitation of salts in the soil. Where soils are thin, in areas of outcrop and subcrop, and the A-soil horizon lies directly on the C-horizon the top of C-horizon is best used.

Sample collection after long dry periods is always better than after a wet spell when salts may have been leached from the soil. It takes time to re-accumulate these. Follow-up sampling conducted immediately after a the wet season in Northern Australia would likely deliver significantly different values than at the end of the preceding dry season. The anomalous signature pattern will be still be present but the magnitude of values may be quite different due to dilution or dissolution and removal of salts in the soil. This also applies to BLEG stream or soil surveys. This fact is often never considered in "total" surveys, with low order values affected by "flushing" likely to be in the BLD range or placed in the background population.

Sample Preparation

Total or near-total geochemical extractions have usually been performed on milled samples, to increase the speed and completeness of digestions. With the aim of many selective extractions to attack loosely-bound metals or coatings of secondary carbonates or Fe+Mn oxides on other mineral grains (while limiting the ionic strength of the resulting solution ionic strength to minimise detection limits), digestions are typically conducted on un-milled samples.

A leach should be capable of buffering the soil pH over the period of the leaching. If soil buffers leach pH, (different soils different pH), reaction process may vary over time and this has an impact on amount of leaching achieved in different media. Variations in selective extraction results may be entirely due to differences in bulk sample mineralogy, rather than actual differences in trace element concentrations in the components of interest. An option may be to remove the components in a sample that unduly affect solution chemistry (such as pH) through application of a pre-leach.

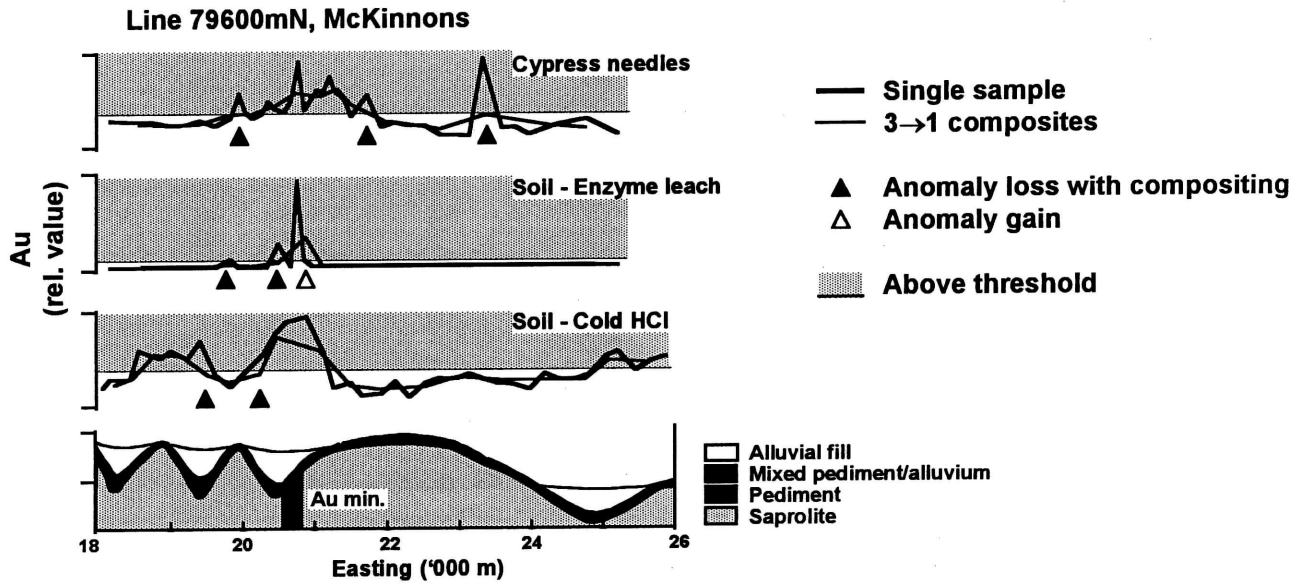


Figure 1. Comparison of single sample and composite sample Au values in Cypress pine needles and the Enzyme Leach and cold 6 M HCl-extractable components of -180µm soils from line 79600N, McKinnons.

DATA PROCESSING

Whereas aspects of the treatment of selective extraction geochemical data follow on from the methods applied to total or near-total geochemical data, differences in the approach to data processing may be required for some selective extraction data sets. This includes the approach to the setting of threshold and in anomalous pattern recognition.

The background values of a suite of samples from total assays are often considered to be uniform, with a single threshold value often chosen irrespective of local variations in lithology and regolith. These variations are difficult to measure as the detection limits for total values are too high in many cases or we do not look closely enough at how the background values are varying with respect to lithological change. Selective leach methods, with their very low limits of detection, measure background variation and this can be seen in line profile data as changes in the magnitude of apparent "noise" along a line (Fig. 2). We are so used to seeing flat, essentially featureless, backgrounds from total assay methods that when presented with the real character of background populations from selective leach data we tend to blame the method rather than acknowledge the real-world variation in geochemistry signatures. Many resort to despair rather than braking the data down into domains and setting thresholds.

Further problems exist in the evaluation of orientation survey data if insufficient samples are collected from true background areas. This can result in an underestimation of the extent of background fluctuations and insufficient data to examine the statistical characteristics of the background population(s). To define an anomaly, you need first to be able to reliably define background. In many situations, slight but significant perturbations in background are suppressed by the linear scaling of data that includes the occasional screaming anomaly and the lack of truncation in graphs of very high values (Fig. 3).

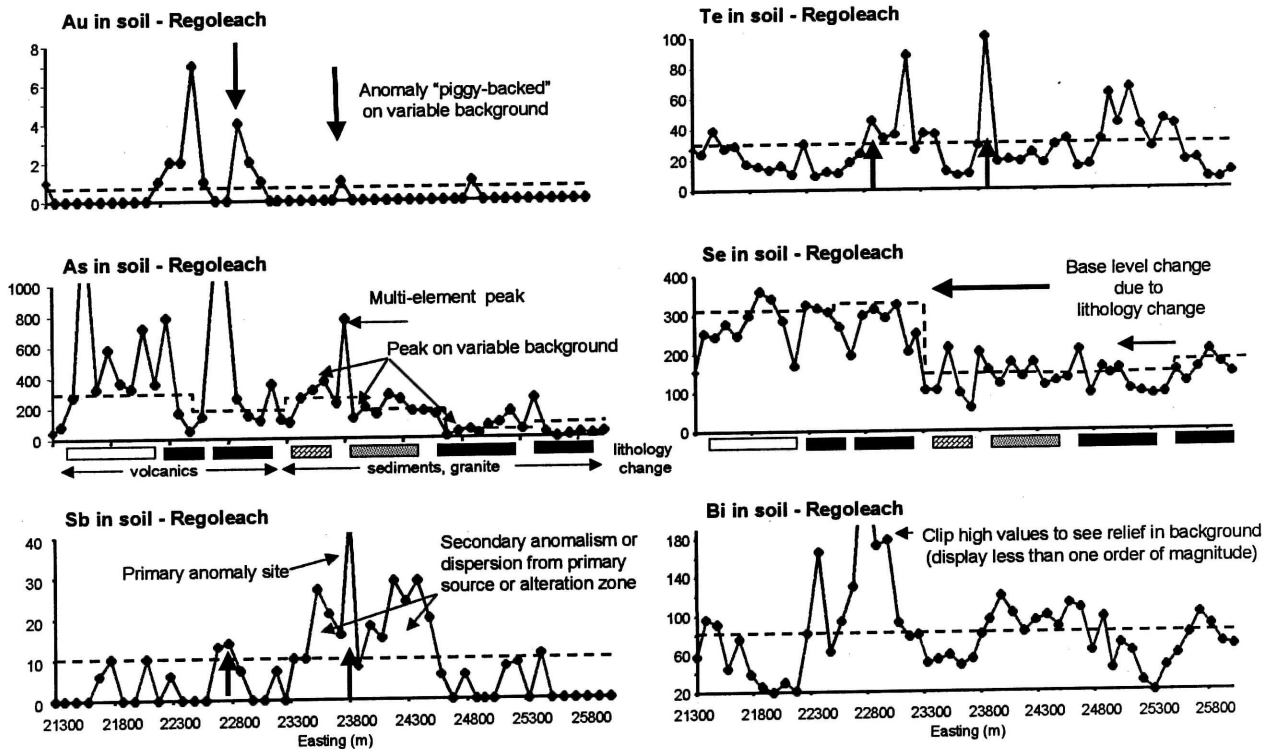


Figure 2. Effects of lithology changes on Regoleach background levels.

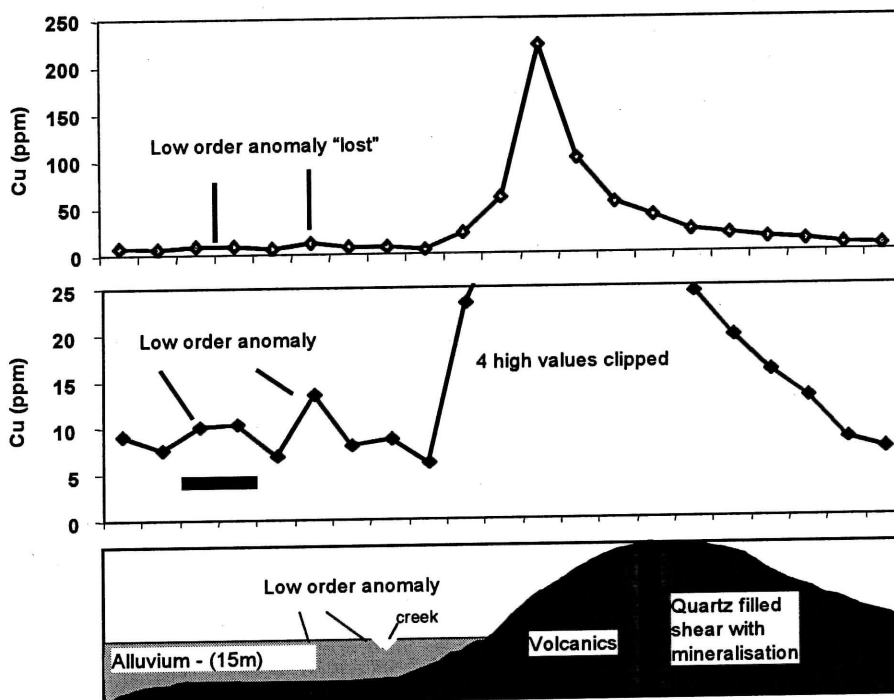


Figure 3. Effect of truncating highly anomalous values in profile plots, to permit observation of low order anomalies.

When merging selective leach data (or any geochemical data) from different batches, it is important to recognise differences introduced by the "background shift" between batches. In the absence of in-house reference materials for use in the more subtle selective extraction techniques, adjustments can be achieved using percentile matching between batches. The background shift may not be entirely laboratory-induced, however, with some suggestions that transient, outer-halo anomalies display seasonal variations.

The absolute value of an element does not necessarily reflect its significance for mineralisation for unexposed mineralisation. In most geochemical surveys people assume that anomalism and mineralisation go hand in hand and that mineralisation is closest to the anomaly peak. This is a reflection of the simple methods by which data is processed without due regard to sample environmental variation and the processes of geochemical dispersion that have transported and then fixed elements emanating from mineralisation. With selective leach methods, most authors tend towards the conclusion that "co-anomalism" of groups of associated elements is an important factor to consider in classifying anomalies, rather than absolute magnitude of individual element values. For example, it might be expected that Cu, Pb, Zn and Ag would all be all anomalous in the vicinity of base metal mineralisation. Gold, As and Ag would normally be expected to be co-anomalous near a mineralised quartz vein system. In a similar manner certain element associations reflect attributes of the superficial environment or regolith; in zones of intense ferruginisation, Co, Ni, As and Zn can often be enriched to a far greater extent than Cu and Pb. Such relationships may be discerned using regression and related statistical methods.

It needs to be recognised that the source of any partial or selective leach or ion exchange anomalism may be either from depth, from beneath the anomaly, or laterally to the side of it. There is no way to discriminate the source other than eliminating or at least accounting for a lateral source when assessing the significance of anomalism. It is very common to find that, even in deeply weathered terrains, the source of partial or selective leach anomalism is a narrow outcropping or sub-cropping quartz vein or quartz float carrying minor mineralisation. Mapping occurrences of such features (as quartz float abundance) and plotting the distribution of them is important.

Whereas totals often display strong correlations between Fe or Mn and other trace elements (hence, the use of regression analysis in anomaly definition), for many of the weaker selective extractions, such as Enzyme Leach and weak hydroxylamine.HCl, there is commonly a poor correlation between trace metals and the major cations of the "carrier phases" digested. The lack of correlation between trace elements and major cations, suggests a number of (as yet untested) explanations:

- i. the transitory or amorphous phases are not saturated (in disequilibrium) and the only control is on the maximum amount of trace elements.
- ii. a lack of specificity in the phases attacked by the digestions, with a small proportion of those digested containing the bulk of the trace elements of interest and the remainder deficient in such trace elements.

In many cases (including those described below), the [trace element]/[major cation]ratio changes markedly during the course of digestion. Such observations raise the question as to whether all selective extractions should proceed to the (notional) point of completion or be halted at an intermediate stage to optimise geochemical contrast and limit the mixture of phases that have been attacked, especially by the weaker digestions.

Further to this, geochemical variation between mineralized and background samples may not just be a function of variations in trace element concentrations but also the distribution of trace element within phases – a higher proportion of the total trace element content residing in secondary and amorphous phases reflecting recent hydromorphic or atmimorphic dispersion haloes. Partial, selective leaching procedures, may provide a means of enhance geochemical contrast in exploration geochemistry, although biases may arise where samples display wide variations in the abundance of

amorphous phases, or where the ambient conditions under which samples are digested are not adequately controlled.

There are few published examples from deeply weathered terrains where selective extractions (especially Regoleach) did not “see” or produce an anomaly where an anomaly existed in the total or near-total assay. The opposite is also commonly the case. The value judgement as to which techniques are most efficient at detecting mineralisation therefore boils down to the old exploration geochemical paradigms:

- Anomaly contrast
- Anomaly continuity
- Anomaly width
- Stable background
- Multi-element support

Some leach methods are more responsive than others for different elements and under different site conditions.

SELECTIVE EXTRACTIONS AS GUIDES TO DISPERSION PROCESSES

In terms of spatial pattern recognition, various models explaining the spatial relationship between selectively extracted trace elements, soil pH, Eh, various gases and even natural electrochemical cells, have been proposed (Clark, 1993; Smee, 1998a,b). Such models indicate the likely development of both an inner halo (directly related to the trace elements escaping from mineralised source) and an outer halo (related to changes in the local environment indicated by the presence of mineralisation but not necessarily characterised by elements showing strong elevation in the mineralisation itself). With the availability of multi-element data, the trace element patterns of such outer halo systems may be more easily detected. It is difficult to apply classical geochemical data interpretation practices and halo models in “outer halo” environments as these are in detail poorly known by the exploration industry for terrains found throughout much of Australia.

In some regolith materials the amount of background component extractable by some selective leaches will be minimal because of a lack of weathering. Conversely, for a highly weathered sample, the original trace element background signature may be completely removed and only metals brought in by ground water and other vectors are likely to be present. The highest leachable background components are likely to come from areas of moderate weathering where the underlying rock is actively breaking down. This may explain the apparent greater success of some selective extractions in glaciated terrains compared with deeply weathered and arid terrains. Further the local pH and Eh will influence the manner in which ions in solution are “captured” by a substrate or released by particular leach regimes.

Partial leach data tends to be more “peaked” in character and show a marked increase in “profile noise” about the position of mineralisation or toward a source (and to some extent also in conventional data) probably reflecting a greater abundance of weakly attached ions as compared to further from source where these ions become more tightly bound or fixed to the substrate. Where ground water is enriched in carbonate or Fe-oxides there can be precipitation of metal ions as carbonates or attached to amorphous Fe-oxides at sites such as the base of dunes, scree slopes or breaks in hill slopes.

Fault zones form significant hydrological barriers to ground water flow. The flow is often deflected to the surface along fault zone, in particularly where there is silicification. Sites adjacent to faults and seepages often show well developed partial leach anomalies (by any method) due to this egression of ground water. Field mapping can assist with sorting this problem out.

Most detectable Au values using the weaker selective extractions should be regarded as anomalous. If Au is not accompanied by common associate elements, such as As, Te, Sb, Ag or base metals, it can generally be considered to be alluvial and likely remote from source. Conversely very low values or lack of gold values in samples high in these associate species should not necessarily be regarded as negative for gold. The fluids that move elements such as Te, Sb etc are capable of transporting gold as well, but only if gold occurs in the source rocks from which these other species were derived. In general gold derived by weathering of sulphide sources is well dispersed, often as atomic gold or sols etc, and is able to be readily detected by Regoleach and some other leach (and BLEG) method. Repeat sampling of soils from such environments generally repeats the gold anomalism. Repeat sampling in alluvial environments generally produces erratic results whether or not you are using BLEG, other selective leaches or total gold methods.

It is important with selective leach data to assay for a range of "atypical" elements to assist in interpretation of the data. Selective leach analysis offers considerable advantages over conventional soil assay methods largely due to its much greater sensitivity. However this greater sensitivity is also much more likely to be influenced by superficial factors, (or at least you see the effects of this more obviously), and these need to be assessed by assaying for a number of elements that most strongly influence surface geochemistry or at least reflect it. The most important elements in this regard are iron, calcium (calcretes), sodium, magnesium, and sulphur (sulphate e.g. gypsum). The presence of iron oxides, calcretes or gypsum gives an indication of likely soil pH values, or sites with seepages. This in turn influences the dispersion, or lack of dispersion, of "mobile" elements transported in ground water.

Example: Reaction Rates for Selective Extractions, Ruby Star Deposit, Arizona.

The time dependence of element release for some common selective extractions has been compared, using soil samples from the Ruby Star Cu deposit, Arizona. This deposit is contained within a large carbonate and volcanic slump block that lies within and is buried by up to 300 m of recent gravels. A suite of soil samples 23 samples, collected above mineralisation and at background sites, was subjected to progressive dissolution over periods ranging from 7 to 1000 minutes.

Patterns of Cu release for the high (> 1%) and low carbonate samples were similar (Fig. 4). Distilled water, magnesium chloride and Enzyme Leach (ENZ) commonly displayed an initial rise (up to the 15 or 30 minute mark) followed by a decrease to the 60 min and then a second period of increase up to the 1000 minutes. Sodium acetate patterns varied with some samples displaying little increase beyond 60 minutes, others a gradual increase to 1000 min and 8144 a decrease between 7 and 30 minutes. For most samples, weak hydroxylamine.HCl displayed a slow rise to 60 min (where the amount released appeared equivalent to the 7 min mark on the strong hydroxylamine.HCl) then a more pronounced rise to the 1000. Total weak hydroxylamine.HCl (CHX) was around 15 to 25% strong hydroxylamine.HCl (HXL) and strong hydroxylamine.HCl was subequal to aqua regia. Cobalt concentrations were relatively low, resulting in DL problems for distilled water, magnesium chloride and for the low carbonate samples sodium acetate. Enzyme Leach displayed a progressive rise to around 240 min for the high carbonate samples and even more pronounced rise for the low carbonate sample (0.08 to 0.2 ppm). CHX showed a distinct change in release at 60 minutes. For the high carbonate samples, aqua regia released more than strong hydroxylamine.HCl, whereas the total releases were similar for the low carbonate samples.

Trace elements were also ratioed against the principal cations of the minerals for which the digestions were targeted. For ENZ, metals were ratioed against Mn, and for CHX against Fe (Fig. 6). The dissolution patterns varied between elements and carbonate contents. In the high carbonate samples, Pb, Co and As displayed a decreasing ratio to the 30 minute mark followed by an increase, whereas Zn generally just decreased. Nickel increased from 7 to 15, decreased to around 30 then increased again, whereas Zn increased marginally to start then decreased to 1000 minutes. The patterns had stabilised by 240 minutes in most cases. In the low carbonate samples, the patterns were similar, except the Metal/Mn ratios tended to be much higher in the first 15 minutes. In the high carbonate samples, the Metal/Fe ratio for weak hydroxylamine.HCl attack generally decreases by an order of magnitude over the first 60 minutes of reaction but stabilises beyond that time. In the case of Ni and to a lesser extent Zn, this trend reverses around the 60 minute mark and the relative release of those metals versus Fe increases, yielding a J-curve. For the low carbonate samples 8144 and 8145 collected away from mineralisation, most of this suite of metals (apart from As) display J-curves with the Metal/Fe ratio reaching a minimum around the 60 minute mark.

Changes in the patterns of trace element release or metal/major cation ratios indicate possible changes in the phases being attacked by various leaches (Fig. 7). Trends in the release of trace elements by Enzyme Leach and 0.25M hydroxylamine.HCl, for instants, suggest that a transition from dissolution of amorphous Mn or Fe oxides to more crystalline phases after 60 minutes, may have occurred. Digestion by less selective extractants, such as heated 1M hot hydroxylamine hydrochloride or aqua regia, result in more complex patterns of trace element correlations than phase specific extractions, such as Enzyme Leach. This could reduce the effectiveness of statistical techniques in enhancing geochemical contrast.

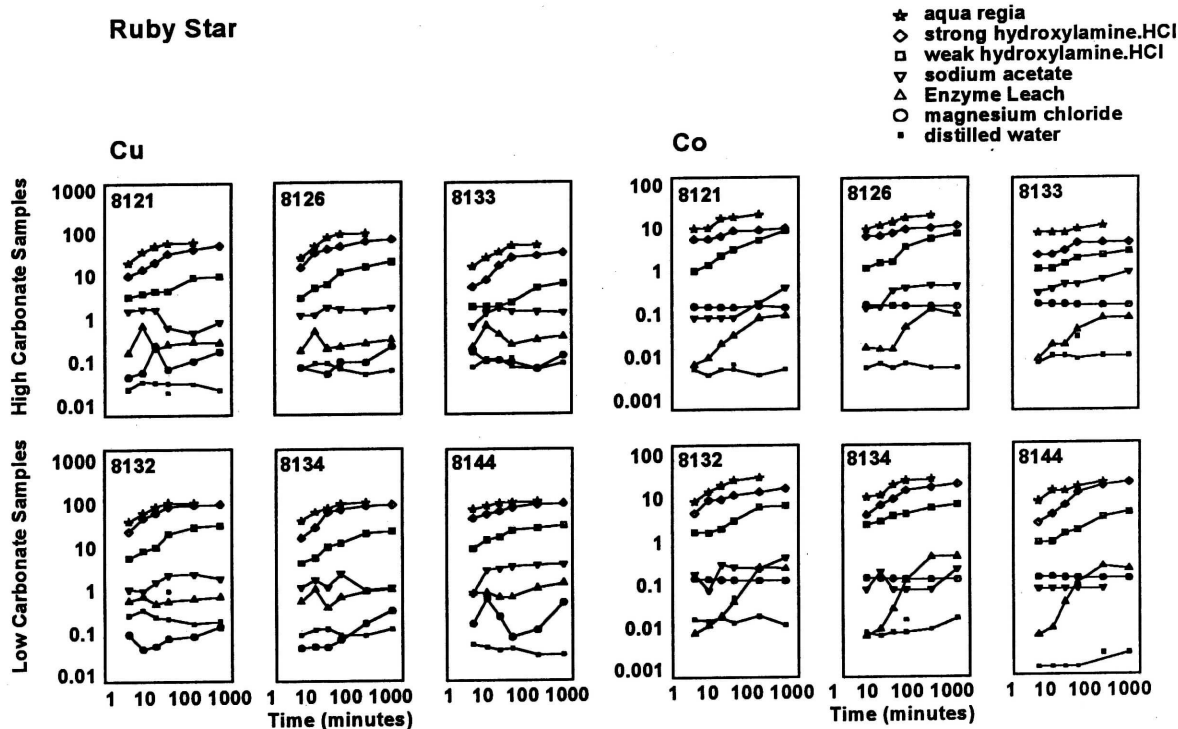


Figure 4. Variations over time in the amount of Cu and Co released from high and low carbonate soils under various selective extractions. Ruby Star, Arizona.

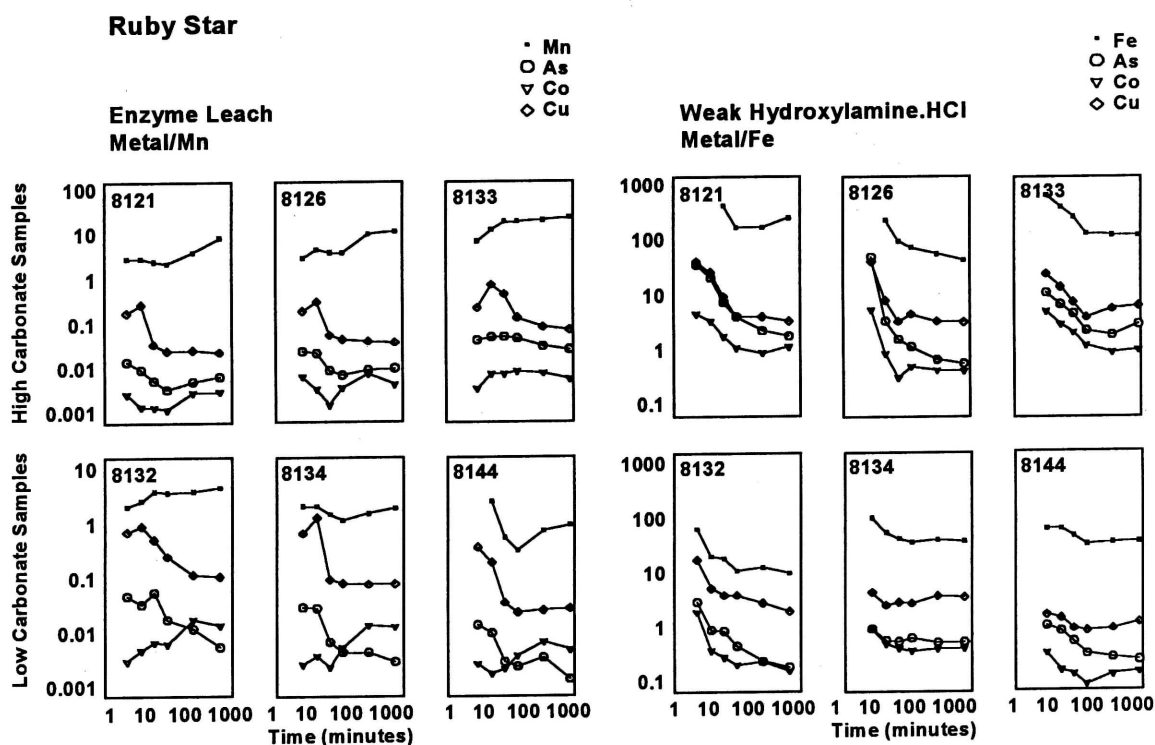


Figure 5. Variations over digestion time for the [metal]/Mn ratios for Enzyme leach and [metal]/Fe for weak hydroxylamine.HCl, for soils from Ruby Star, Arizona.

Peak geochemical contrast between samples from over mineralised and background sites for some of the selective extractions is observed in the early stages of digestion, often within the first 15 to 30 minutes. It is not clear if the observed geochemical contrast is merely the result of high carbonate contents in soils overlying the Cu mineralised block. The relative rates of digestion between trace elements and major cations indicates enrichment of Cu, Co, Zn and other metals at the rims of secondary Fe and Mn oxides, especially in the vicinity of mineralisation, but uniform distributions through the carbonates.

ENZ digestions on samples following removal of carbonates by sodium acetate and the continuing dissolution trend for many elements in leaches such as CHX, indicates either incomplete attack on the phases for which these digestions are designed or that leaches progress to more crystalline forms of Mn and Fe oxides once the less crystalline or amorphous phases are removed. This is also suggested by the trends for major and trace elements in the ENZ and CHX digestions (Fig. 6). For ENZ there was an abrupt increase in Fe and Zn release after 60 minutes, yet a plateau in Mn release. For CHX there were more subtle changes in the rate of release of Fe and Mn after 60 minutes, but very abrupt changes in the release of Zn, Cu and other trace elements, together with the Cu/Fe and Zn/Fe ratios. In both cases this may indicate transition from digestion of amorphous phases to attack of more crystalline phases.

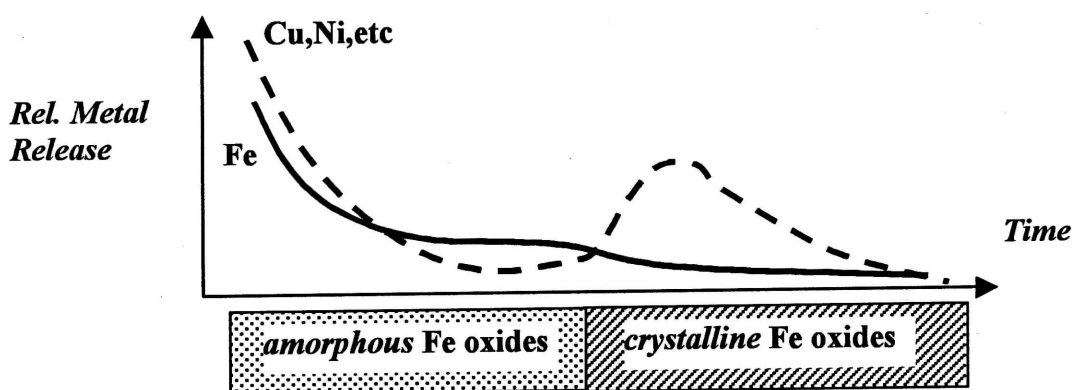


Figure 6. Schematic relationship between the progressive relative release of trace elements and Fe from amorphous and then more crystalline phases.

The patterns of digestion suggest that in both amorphous and crystalline Fe oxides, Cu, Zn, and to a lesser extent Co, Pb are relatively enriched on the rims of the phases. This feature is less prominently developed for the amorphous Mn oxides. For both oxides, the rim enrichment is more pronounced at the mineralized sites. Such patterns have been observed for the dissolution of ferruginous lags and gossan fragments (Alipour *et al.*, 1995; Xie and Dunlop, 1998).

Example: Comparison of Vegetation, Lag totals and cold HCl extractions, Cobar.

In the Cobar area (NSW, Australia), detection of mineralization using conventional soil sampling and total metal analysis is impeded. This is due to the intense leaching of trace elements within the weathered profile, discontinuous coverage of transported materials and the existence of diffuse regional geochemical anomalies of ill-defined source. Selective chemical extractions, applied to various regolith components, and biogeochemistry offer a means of isolating localised geochemical patterns related to recent dispersion of trace elements through the overburden.

Lag geochemical patterns across the McKinnons deposit (Au) and Mrangelli prospect (Pb-Zn-As) reflect mechanical dispersion processes and minor hydromorphic effects. Concentrations of more mobile elements tend to be higher in the non-magnetic fraction, due to higher proportions of goethite and poorly crystalline hematite than in the magnetic fraction geochemical responses for metals extractable by cold 40% hydrochloric acid (CHX) and total soils reflect the leached nature of the residual profile, low grade of mineralization, dilution by aolian components and disequilibrium of fine fractions with coarser, relict Fe-oxides. The stronger contrast for CHX for most metals, compared with total extraction, indicates surface accumulation of trace elements derived from underlying mineralization.

Enzyme leach element anomalies are intense but generally located directly over bedrock sources or major structural breaks, irrespective of the nature of the overburden. Though mechanisms for the dispersion of trace elements extracted by enzyme leaching are not well established, the lack of lateral transport suggests vertical migration of volatile metal species (atmimorphic dispersion). The strong, multi-element response to mineralization in the cypress pine needles indicates significant metal recycling during the present erosional cycle. However, a comparison of the trace element concentrations in vegetation (cypress pine needles) and selective extractions of soils, indicates that recycling by the plants is not the dominant mechanism for transportation of metals through the overburden. The vegetation may be responding to hydromorphic dispersion patterns at depth. The use of selective extractions may be useful in detecting mineralization through deeply leached profiles, but offers even greater potential when integrated with biogeochemistry to detect targets buried by substantial thickness of transported cover.

On lines A and B, both magnetic and non-magnetic lag display a series of spot Au anomalies (7-10 ppb), extending east from the main north-east trending mineralized zone (Fig. 7). A similar pattern is observed in the total Au contents of the adjacent soils, though anomalies on line A are restricted to the zone of mineralization and adjacent drainage. On line A there is a contiguous set of weak hydroxylamine.HCl (CHX) Au anomalies (0.3-0.7 ppb), extending 250 m either side of the projection of the structure hosting the mineralization. CHX Au values are slightly elevated in the drainage on the eastern end of the line, and in general, appear to be slightly elevated across the alluvium filled channels. A spot enzyme leach anomaly of 1.2 ppb occurred above the trend of mineralization, with a subsidiary peak in the adjacent drainage. A consistent, 2 km wide Au anomaly is observed in the cypress pine needles. Concentration peaked at 4.2 ppb (above a background of 0.8 ppb) and the anomaly is centred on the projection of the McKinnons mineralization. The Au spike in the needles at 23400E, located at the top of a low ridge, cannot be related to known mineralization.

The weak-to-moderate spatial correlation between the trace element contents of the non-magnetic lags and the CHX extractable soils at McKinnons and the slight broadening of the anomalous zones for CHX compared with the totals for soils around the main anomalies (also observed in the Fe-contents), suggests that a portion of the amorphous Fe may be derived from the degradation of adjacent lags and subsequent dispersion in surface soils. In most instances, CHX geochemical anomalies developed above mineralized zones are more extensive than those displayed by the total metal contents of the soils.

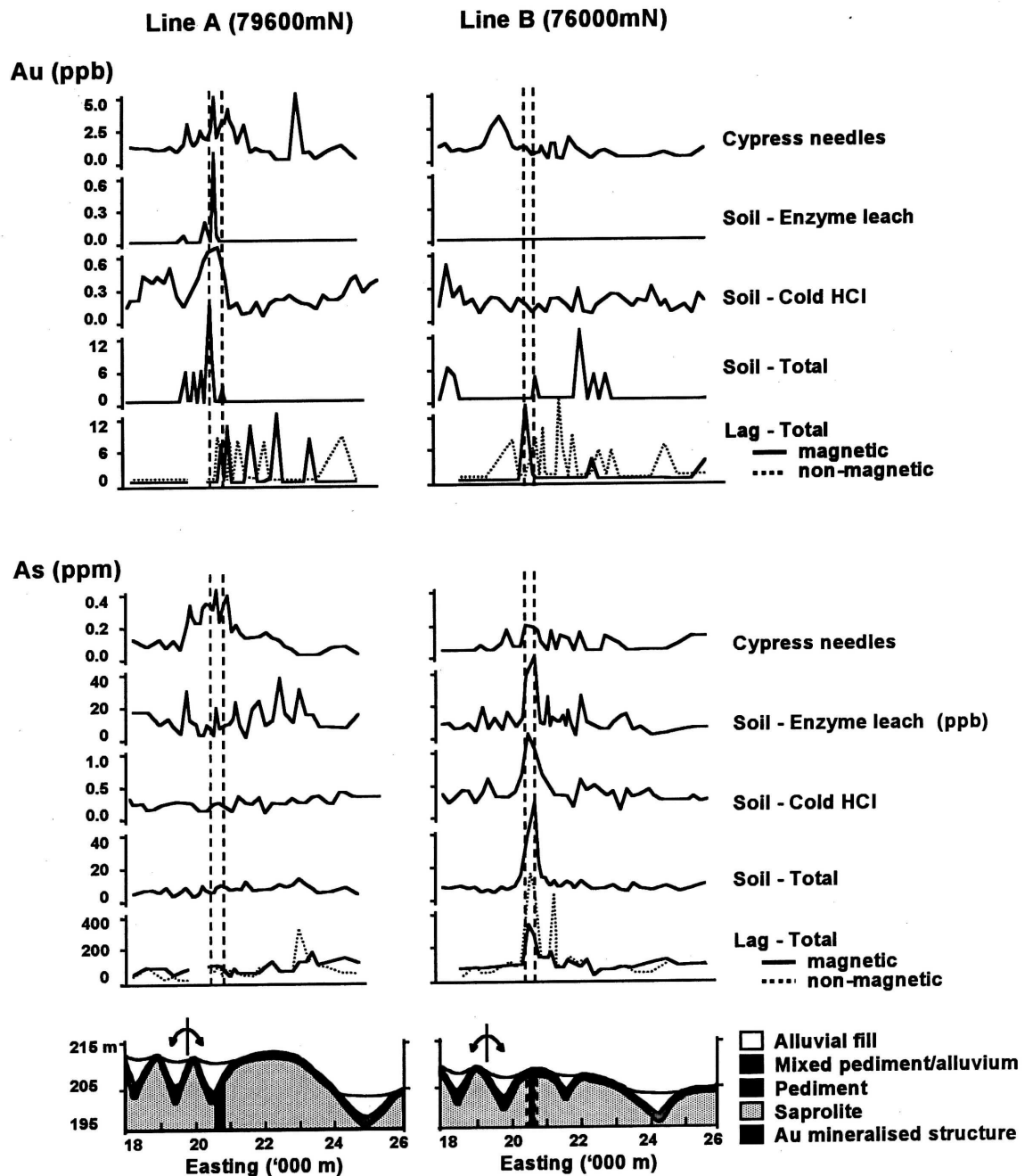


Figure 7. Comparison of the total Au and As contents of Cypress pine needles, magnetic and non-magnetic lag and soils with the Enzyme Leach and cold HCl extractable contents, Lines 79600N and 76000N, McKinnons deposit, Cobar, NSW.

The relationship between Fe and Zn concentration of the non-magnetic lags, total and CHX extractable soils is presented in Fig. 8. Zinc is weakly correlated with Fe in lags, more strongly correlated in the total soils, but uncorrelated for the CHX extraction. follows the trends observed at Mrangelli and other sites in the region by Alipour *et al.* (1997). The poor to insignificant correlation between trace elements and Fe in CHX extracts precludes direct application of regression against Fe to enhance anomaly patterns. Progressive leaching of unpulped lag clasts in 6M HCl indicates that Pb, Mn

and Zn in non-magnetic lag are preferentially concentrated at the grain rims relative to the cores (Fig. 9). The molar ratio of Pb to Fe dissolved decreased significantly from an initial high after 30 minutes of leaching towards a minimum beyond 30 hours. In all sample types for Cu and for Zn in the magnetic fraction, there was little initial metal release.

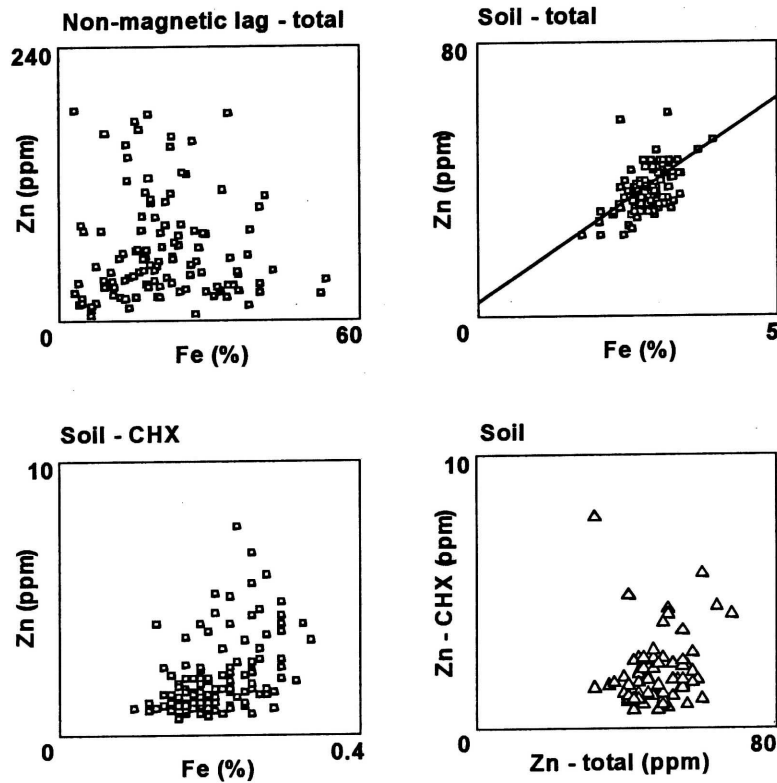


Figure 8. Correlations between trace and major element concentrations for soils under various extractions, McKinnons deposit, Cobar, NSW.

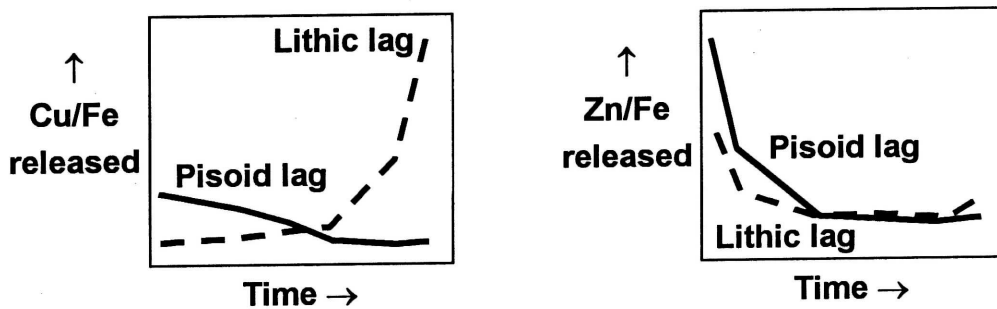


Figure 9. Time variation in the ratio of Cu and Zn to Fe for pisoid lags and lithic lags from Cobar, under 6 M HCl leach.

RESEARCH DIRECTIONS

It is important that the "black box" aura, which surrounds many selective extraction methods, be eliminated. Whereas empirical case studies are assisting in the development of selective extraction techniques, more fundamental questions of "mechanism" need to be addressed such as:

What are the potential effects of variations in sample processing and digestion on trace element release. This includes the problem of uncontrolled temperatures on leach efficiency, the ideal sample size to balance representivity with physical problems such as readsorption.

What are the mechanisms by which trace elements disperse in the secondary environment in arid terrains?

In what form are such trace elements bound in regolith?

Does the form of such metals alter over time and at what rate?

To what extent are existing selective extraction methods able to isolate the trace elements associated with various minerals and other regolith components?

What new or modified extraction procedures might be more specific in the components attacked?

For most selective extractions, the actual effects of different leaches on the various mineral phases (especially those that host trace elements dispersing from mineralisation) is poorly understood, as is the effect of variations in mineralogy (including the proportion of different minerals, crystallinity, mixed-phases) on the efficiency and specificity of such extractions.

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