

## EXTRACTION TECHNIQUES IN EXPLORATION FOR BURIED MINERALIZATION, CURARA WELL, WESTERN AUSTRALIA

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### ABSTRACT

At the Curara Well Au prospect, about 420 km NNE of Perth, WA, primary and lateritic gold mineralization are overlain by up to 20 m of barren transported overburden. A previous study conducted for CRAE had suggested that mobile metal ion (MMI) extractions of soils located buried mineralization. The site was therefore selected for a series of investigations of this and other partial and selective extractions in delineating buried mineralization. Soil samples were collected from one profile and eight traverses in mineralized and background areas and were treated using various commercially available and in-house analytical extraction techniques.

The sequential selective extractions involved pH 5 acetate (for carbonate and adsorbed metals), followed by 0.1 M hydroxylamine (Mn oxides) and 0.25 M hydroxylamine ('amorphous' Fe oxides). As expected, most of the extractable Mn is dissolved with the 0.1 M hydroxylamine, with Co and (in part) Ba and Ni. Extractable Mn correlates with extractable Fe, even though they are dissolved by different reagents, indicating an indirect secondary origin for these two phases (e.g., surface drainage depositing Mn and Fe, or biological effects). Accordingly, other metals (REE, Cu, Pb and Zn) correlate with Mn, even though they are hosted by amorphous Fe oxides.

The partial extractions used were 4 M hydrochloric acid (HCl) (15°C / 4 hours), mobile metal ion (MMI) extractions and Enzyme Leach. There was good agreement between the combined results for the sequential selective extractions and the HCl extractions for most elements, despite only a very minor proportion of the total Fe being dissolved, indicating that these extractions are dissolving Mn oxides plus specific Fe-rich components, be they separate minerals or disordered mineral surfaces. MMI concentrations were generally lower than for the sequential or HCl extractions, approximate proportions (MMI/HCl) being Co (0.05, though variable), Cu (0.1), Pb (0.1), Ni (0.4), Zn (0.5), Cd (1) and Ag(1), though with similar spatial distribution patterns. The Enzyme Leach concentrations were lower again than MMI: Cd, Cu, Pb and Zn had generally 10% as much extracted by Enzyme Leach as for MMI, with a linear ratio; whereas there is a poor correlation though a higher Enzyme Leach / MMI ratio for Ag, Co and Ni.

Soils overlying mineralization contain relatively high concentrations of extractable Ba, Be, Cd, Co, Cu, Ni, Pb, REE, U and Zn for most to all of the extractions and for As, Au, Cs, Ga, Hg, Mo, Nb, Sn, Te, Th and Tl for one or some of the extractions. Different techniques were optimal for various elements (e.g., MMI gave the highest contrast for Cu over mineralization, with no enhancement for Co and Ni). The best anomaly to background contrast was obtained from extractable Mn, which exceeds 800 ppm over mineralization, with a background of near zero, whereas amorphous Fe has a maximum of 700 ppm, with a 200 ppm background.

However, similar anomalies are observed elsewhere in the study area, correlated with drainage zones, and the higher concentrations of extractable base metals above mineralization are primarily due to association of these metals with Mn oxides and/or amorphous Fe oxides. The MMI-extractable metals showing high contents over mineralization (e.g., Cu and Cd) were also associated with these phases. This suggests that this spatial correlation of extractable (and, weakly, total) metals with the buried Au deposit is coincidental. Similarly, there is unlikely to be a direct link between the surface Mn anomaly and the buried Au mineralization 10-20 m below. Surface phenomena, unrelated to the presence of mineralization, such as the present-day drainage, are possible causes. It is considered that partial extractions can only be understood and interpreted correctly if conducted in conjunction with an understanding of locally critical soil phases such as Mn oxides, amorphous Fe oxides, carbonates and any other materials likely to adsorb or otherwise accumulate dissolved ions. Additionally, this project points to the need for proper orientation or baseline studies before attempting to apply novel techniques or interpret data.

## INTRODUCTION

Over the past few years selective extractions have regained popularity as a technique for the discovery of buried mineralization. If effective, they would offer an inexpensive and easy method for exploration in areas of transported overburden and assessment of the utility and range of these methods is therefore critical. This paper focuses on the use of selective extraction at Curara, which has Au-rich laterite covered by up to 20 m of transported overburden in a relatively undisturbed site. The investigations have been conducted in order to determine: 1 whether soil extraction anomalies exist over buried mineralization; 2 whether these anomalies be observed using different techniques; 3 is the primary cause of the anomalies.

The aim of selective extraction is to dissolve particular soil phases in a controlled manner, and the resulting solutions analysed for trace elements of interest. These techniques can be used to investigate how trace elements are distributed between the phases. In addition, these extractions have been used in the past for geochemical exploration because it has been perceived that elements associated with mineralization (especially those hosted by sulphides) are more likely to be released during weathering than those in barren rocks (hosted by silicates), more widely dispersed, and more probably held by secondary minerals and hence likely to be preferentially released by extraction solutions. In contrast, some of the new extraction techniques currently used for geochemical exploration are partial rather than selective digests: i.e., they extract part of a phase or phases, rather than a selected mineral. These new methods are being claimed to be highly effective in the location of buried or otherwise hidden orebodies, and there has been a high degree of interest in their application. It is important to examine the chemistry of partial/selective extraction and the mineralogical implications more fully.

In addition to examining these new methods, standard extraction solutions were used to test for easily extractable ions and ions associated with Mn oxides and/or amorphous Fe oxides. These phases are commonly thought to influence the mobilities of a wide range of metals and pathfinder elements and may be important controls for the metals and elements commonly determined in commercial partial leach techniques. The scope of this study at Curara includes the correlation of selective extraction results with the underlying mineralization, effect of Mn oxides and amorphous Fe oxides on extractability of various base metals and investigation of other partial leach techniques.

## SITE STUDY AND METHODS

### SITE CHARACTERISTICS

The Curara Well Au prospect is located some 420 km NNE of Perth, WA (Figure 1). It is situated within the Wydgee Fold Belt immediately south of the Mount Magnet Greenstone Belt. The area is approximately 100 km N of the Menzies Line, a narrow east-west transitional zone across which there are marked changes in soil types, vegetation and groundwater quality (Butt *et al.*, 1977). Outcrop is extremely poor (< 1%). Initial exploration identified a possible 100,000 oz laterite resource overlying mineralized bedrock, with a total resource of 520,000 oz defined in 1995 (Sons of Gwalia, 1997). The prospect is located over a tonalitic porphyry stock that is bounded on its eastern side by a package of mafic amphibole schists. Detailed aeromagnetics have shown that the porphyry stock is cut by a number of NW-NW trending fault splays off a regional shear that occurs to the east of the prospect. The laterite mineralization straddles one splay in particular, and the greatest tenor of mineralization is developed where a wedge of porphyry has been faulted out from the main body of the porphyry stock by this splay. The present day broad and shallow drainage system over the mineralized zone also follows this fault splay. Bedrock mineralization is present within both the porphyry fault wedge and the hanging wall mafic schists immediately to the east. The Au mineralization shows some association with thin (< 1 cm) quartz-actinolite veins. The overall percentage of sulphide (pyrite±pyrrhotite and trace chalcopyrite) associated with the mineralization is low (< 3%) (David Hamdorf, CRA, Personal communication).

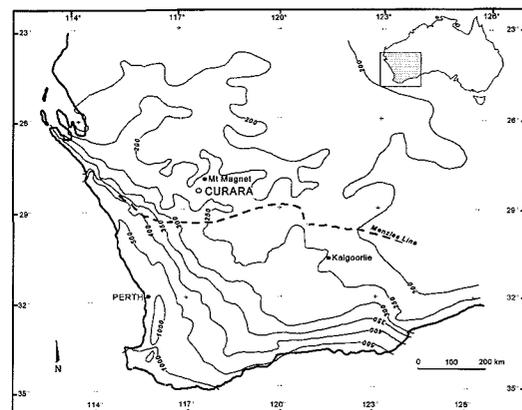
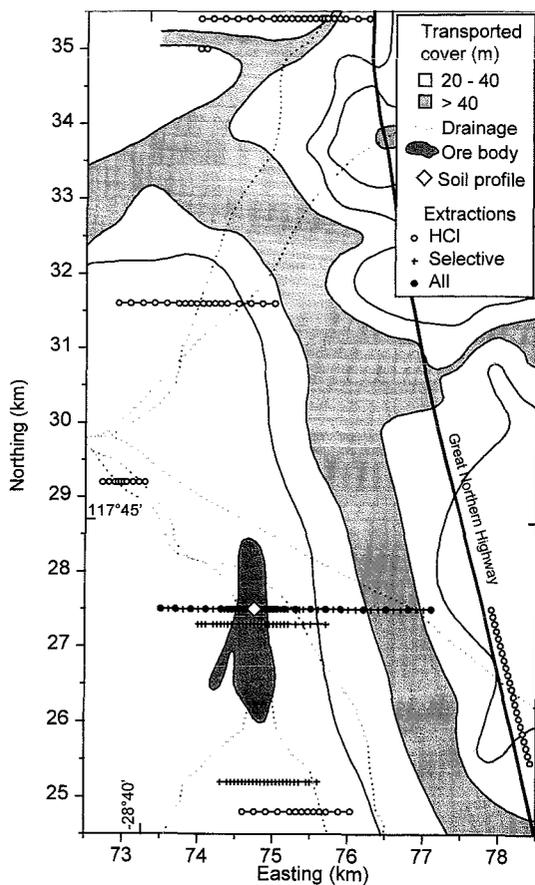


Figure 1: Location of the Curara Well Au prospect, with rainfall in obytes (mm/yr) and the approximate position of the Menzies Line

The majority of the prospect is covered by 0 - 50 m of alluvium and hardpanized colluvium (Figure 2), and some 30 - 60 m of partially preserved lateritic weathering profile. The buried laterite profile is generally stripped back to lower laterite, mottled zone or upper saprolite. Much of the laterite mineralization is hosted by nodular mottled zone, with deeper supergene Au enrichment. There is laterite outcrop in the south west corner of the anomaly. Over much of the deposit the laterite is covered by about 10 m of sediments. Laterite Au enrichment well defines the primary mineralization.



**Figure 2:** Sampling traverses for various extractions, Au orebody, drainages and depth of transported overburden at Curara (using data provided by CRA Exploration Ltd and Sons of Gwalia Ltd).

The area has a semi-arid to arid climate, with an average annual rainfall of approximately 230 mm (Figure 1). Rainfall variability is high and results mostly from frontal systems from the west and south-west in winter and from patchy, convectional storms and cyclone-related rain-bearing depressions in summer. Summers generally are dry and hot to very hot; winters are cool to mild, with a few frosts. The vegetation is dominated by mulga (*Acacia* spp.) and by various types of poverty bush and turpentine (*Eremophila* spp.).

### SAMPLE COLLECTION, TREATMENT AND ELEMENTAL ANALYSIS

The first series of regolith samples were collected by CSIRO personnel in late-1993. This involved two traverses at 27300N and 27500N (Figure 2). Sampling at 27500N was done so as to repeat previous samples used for MMI (Mobile Metal Ions; © Wamtech Pty Ltd) analysis conducted on samples collected by CRA staff. The soils were collected by spade, after scraping away the top 1 to 2 cm, including any debris and or humus, to approximately 20 cm depth, and commonly duplicated previous samples taken by CRA personnel for MMI investigations. A soil profile was sampled down to 0.4 m (to hardpan) at 74750E / 27500N. Additional traverse samples were collected in May-1995, extending the 27500N line to the west and east and adding a traverse at 25200N, with several additional traverses sampled in early-1998 (Figure 2).

Selected samples from the 27300 and 27500N traverses and from the soil profile were pulverized to nominal < 75 µm and analysed for Ag, As, Au, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, Ir, K, La, Lu, Mo, Na, Rb, Sb, Sc, Se, Sm, Ta, Th, U, W, Yb and Zn by neutron activation (NAA) and for Zn, Cu, Ni, Ti, V, Mn and Pb, using X-ray fluorescence (XRF) of pressed disks. Samples were sieved to < 2 mm for the extractions described below. Figure 2 shows the locations of samples for different types of extractions.

### SEQUENTIAL SELECTIVE EXTRACTIONS

The three methods detailed below are observed to be commonly highly selective for particular mineral phases in soils (Chao, 1984). Five grams of sample were weighed into a centrifuge tube and then sequentially extracted by the methods described below:

#### pH 5 acetate (carbonates and surface adsorbed metals).

The 5.00 g of sample was shaken with 95 mL 1 mole/litre (M) ammonium acetate at pH 5 for 6 hours. The mixture was then centrifuged (4000 rpm, 15 minutes) and the supernatant decanted. The extraction was repeated. The solid was then mixed with 10 mL 0.1 M ammonium chloride and centrifuged. The three aliquots were combined for analysis by ICP-MS for Ag, As, Au, Be, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Pt, Sb, Se, Sn, Te, Th, Ti, U, W, Zn and Zr.

**0.1M hydroxylamine (Mn oxides).**

The residual solid from the extraction was then mixed with 90.0 mL 0.1 M hydroxylamine hydrochloride in 0.01 M HNO<sub>3</sub> for 30 minutes. The mixture was centrifuged and the supernatant decanted and analysed by ICP-MS for the same suite of elements as the pH 5 extraction.

**0.25M hydroxylamine (amorphous Fe oxides).**

The residual solid from the extraction was then mixed with 90.0 mL 0.25 M hydroxylamine hydrochloride in 0.25 M HCl at 50°C for 30 minutes. The mixture was centrifuged and the supernatant decanted and analysed by ICP-MS for the same suite of elements as the pH 5 extraction.

**HCl EXTRACTIONS**

HCl extractions were performed by Ultra Trace Pty Ltd using their commercially available procedure. Four grams of sample was digested in 8 mL 4 M HCl at 15°C for 4 hours for analysis by ICP-MS for the same suite of elements as the pH 5 extraction, less Cr.

**MOBILE METAL ION ANALYSIS**

The MMI (Mobile Metal Ions; ® Wamtech Pty Ltd) process uses two leachant solutions to dissolve target metals (Mann *et al.*, 1995). The technique involves acid solution analysis by ICP-MS for Cd, Cu, Pb, Zn and alkaline solution analysis by ICP-MS for Ag, Au, Co, Ni, Pd. The extractions and analyses were performed by Analabs Pty Ltd, using approximately 100 g for each of the two extractions.

**ENZYME LEACH ANALYSIS**

Enzyme Leach is a selective leaching procedure utilizing a reaction between glucose oxidase and dextrose to produce low concentrations of hydrogen peroxide to partially leach amorphous MnO<sub>2</sub> (Clark, 1993), prior to analysis by ICP-MS for Ag, As, Au, Ba, Bi, Br, Cd, Ce, Cl, Co, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, I, In, Ir, La, Li, Mn, Mo, Nb, Nd, Ni, Os, Pb, Pd, Pr, Pt, Rb, Re, Ru, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, W, Y, Yb, Zn and Zr.

**RESULTS****COMPARISONS BETWEEN EXTRACTION METHODS****Sequential selective extractions**

The selective extractions are, as the name implies, designed to specifically extract certain minerals or phases (Chao, 1984), and results indicate this has occurred. Note, however, that for a number of elements, particularly REE, Th, and U, only a small proportion were extractable by any reagent, so the comments below are

for the extractable component only. The pH 5 acetate reagent, specifically designed to dissolve carbonates partially (bracketed) or mostly to wholly extract Ba, (Be), Ca, (REE), (Cu), (Mn), Th, U and (Zn). It should not be assumed that all these elements occur within carbonates, particularly given that Ca content is < 0.1% and that exchangeable and surface adsorbed elements will also be extracted by this reagent. For example, U commonly occurs as soluble secondary minerals that dissolve in an acid acetate solution. More Ba was dissolved by pH 5 acetate than by the HCl extraction, possibly due to barite being soluble in acetate (due to complexing of Ba), but not in acid.

The second extraction, 0.1 M hydroxylamine, is designed to dissolve separate phase Mn oxides. Although, as expected, most of the total extractable Mn is dissolved with this reagent, the approximate proportions for extractable Mn being 1:8:1, for pH 5 acetate : 0.1 M hydroxylamine : 0.25 M hydroxylamine. The Mn dissolved by the pH 5 acetate reagent represents highly soluble Mn, either within carbonates, separate-phase MnCO<sub>3</sub>, or particularly soluble Mn oxides. The 10% of the extractable Mn only dissolved by 0.25 M hydroxylamine is presumably Mn within amorphous Fe oxides. Plotting total extractable (the sum of the three sequential selective extractions) vs total Mn (Figure 3) indicates approximately 2/3 of the total Mn to be extractable, with a residual of unextractable Mn of approximately 100 ppm. This effect is observed elsewhere in the Yilgarn Craton (Gray, unpublished results). Other elements partially (bracketed) or mostly to wholly extracted by the 0.1 M hydroxylamine reagent are Ba, Co, Ni, and (Pb). The low number of elements substantially dissolved by this reagent is surprising, given the accepted capacity of separate phase Mn oxides to be major sinks for metals. The extractable Mn broadly correlates with total extractable Fe (Figure 4), even though these two elements are dissolved by different reagents, indicating an indirect secondary cause for the precipitation of these two phases, e.g., due to environmental effects. Thus, a number of extractable metals correlate with total and extractable Mn, even though most of these elements are only dissolved by 0.25 M hydroxylamine and are thus hosted by amorphous Fe oxides.

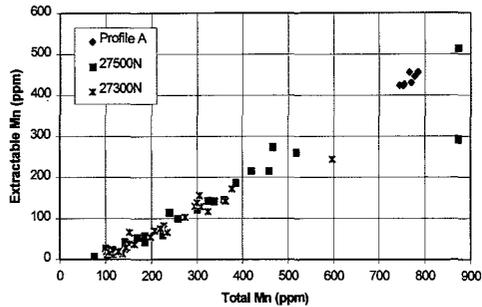


Figure 3: *Sequentially extracted Mn vs total Mn for Curara*

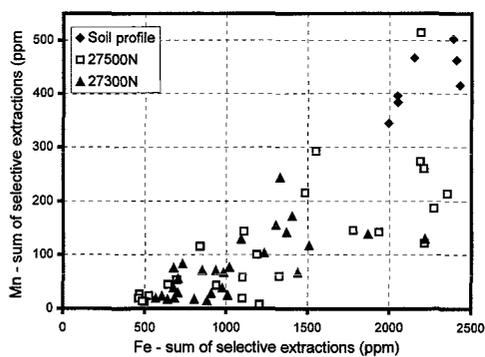


Figure 4: *Correlation between Mn and Fe extracted by the three selective extractions*

Iron oxides can be a significant scavenger of a number of metals and anions, with more amorphous forms, such as ferrihydrite ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ) being particularly active. All of the extractants dissolved small proportions of the total Fe, consistent with Fe being dominantly present as crystalline Fe oxides, such as goethite and hematite. Of the sequential extractants, only 0.25 M hydroxylamine dissolved significant Fe (89 - 98% of the total extractable Fe, though only approximately 0.05% of the total Fe), probably representing amorphous Fe oxides. That this is not a clearly defined phase is indicated by a significant batch effect for the amount of Fe (but not other elements) dissolved by 0.25 M hydroxylamine or (as discussed below) by 4 M HCl. However, the good agreement between the sum of the selective extractions and the 4 M HCl results for most other elements suggests that the extraction is dissolving specific Fe-rich components, be they separate phase minerals or disordered surfaces. Other elements partially (bracketed) or mostly to wholly extracted by 0.25 M hydroxylamine are Be, (Co), Cu, Li, (Mn), Ni, Pb, REE, (U) and (Zn).

### HCl extractions

The 4 M HCl digest dissolves similar concentrations to that of the combined sequential results for all elements for which there are adequate data, namely Ca, Fe, Mn, Ba, Be, Cd, Ce (Figure 5), Co, Cu, Li, Ni, Th, U and Zn. For other elements, the higher detection limits from the solution matrix, plus the cumulative errors, means that the results for the combined sequential analyses are not sufficiently precise for comparison, i.e., the HCl extractions, though in effect giving a "combined result", and therefore giving less information of the mineral association of elements, are more sensitive and precise than the combined selective extraction results. The good agreement between the combined sequential and the 4 M HCl extractions for most elements is consistent with the extraction model illustrated in Figure 6. In general, the poorest agreement between 4 M HCl and the combined sequential results was for Fe, which also showed significant batch effects. This is represented by the double-headed arrow for 4 M HCl in Figure 6, indicating that this reagent in some cases does not dissolve all of the amorphous Fe (defined as 0.25 M hydroxylamine-soluble Fe) whereas, in other samples, it dissolves some of the crystalline Fe. The good agreement between methods for a number of elements associated with amorphous Fe (e.g., Cu and Ni) indicates that these elements are primarily associated with the most soluble, amorphous Fe oxides, rather than with less-soluble Fe oxides.

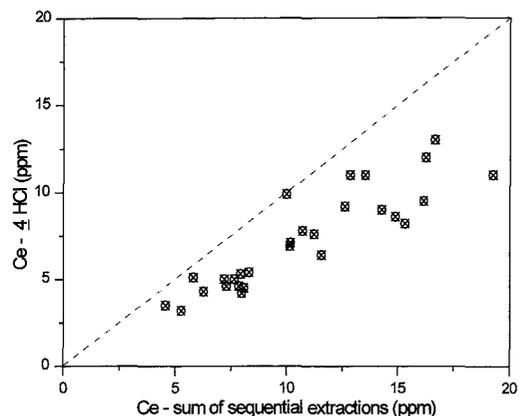


Figure 5: *4 M HCl extractable Ce vs Ce extracted by the three selective extractions for Curara samples. Dashed line represents line of equality*

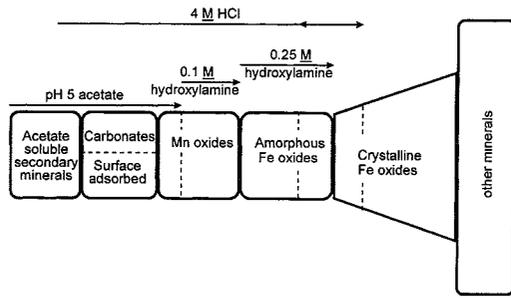


Figure 6: Diagrammatic representation of the phases dissolved by selective and acid extractions

### Mobile metal ions

The MMI analysis is, in fact, two separate techniques (Mann *et al.*, 1995). The first, an acid extraction for Cd, Cu, Pb, Zn, extracts considerably less than the selective or HCl extractions. However, for these elements MMI is to the other methods in terms of comparison between samples (example for Cu given in Figure 7). These results indicate that in this area either selective or 4 M HCl extractions will give comparative results to MMI.

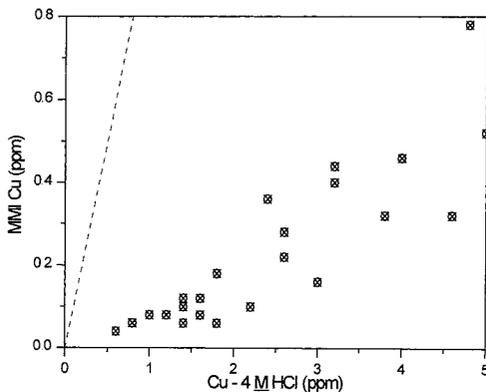


Figure 7: MMI Cu vs 4 M HCl extractable Cu for Curara samples. Dashed line represents line of equality.

The second method is an alkaline extraction for Ag, Au, Co, Ni and Pd. MMI Au and Pd concentrations are below detection at this site and there is no consistent variation in Ag. Probably as a consequence of the alkaline reaction, the Co data are unlike those observed for other techniques, though Ni gives a correlation with 4 M HCl extractions.

The MMI extractions dissolve a significant fraction of the total extractable component. Approximate proportions extracted (MMI/HCl) are Co (0.05, though variable), Cu (0.1), Pb (0.1), Ni (0.4), Zn (0.5), Cd (1) and Ag(1), though with similar spatial distribution patterns. As discussed below, for the later traverses, 4 M HCl extractions were used as these offered good detection limits at low cost.

### Enzyme Leach

The Enzyme Leach reagent is targeted at an 'amorphous' Mn phase, with the proportion of Enzyme Leach to total extractable Mn being about 5%. Other elements did not show any clear correlation with Enzyme Leach Mn, except for Enzyme Leach Co, which correlates with Enzyme Leach Mn. The Enzyme Leach method also appears to give unique results, and also provides a large range of elements. Interestingly a number of Enzyme Leach extracted elements, namely Cs, Fe, Ga, Hf, La, Nb, all REE with significant concentrations, Pb, Sc, Sn, Th, Ti and Zr, show very close linear correlations with each other. Most, but not all, of these elements tend to be high-charge, with only low concentrations (except for Fe extracted by this method). These surprising close correlations suggest either a highly specific interaction between these elements and Fe within those soil phase(s) dissolved by Enzyme Leach or an analytical interference from Fe. This effect should be checked before these elements are routinely used.

For elements dissolved by the acid MMI leach (i.e., Cd, Cu, Pb and Zn), the Enzyme Leach vs MMI plot is broadly linear (example for Zn given in Figure 8), with an Enzyme Leach to MMI ratio of approximately 0.1. For the elements dissolved by the alkaline MMI leach (i.e., Ag, Co and Ni) the Enzyme Leach vs MMI plots show little correlation, although the Enzyme Leach to MMI ratio is higher (Ag and Ni: 0.05 - 0.5; Co: 0.2 - 5). With the exception of the high charge ions mentioned above, most of the elements above detection using Enzyme Leach were greatest for the high-Mn samples.

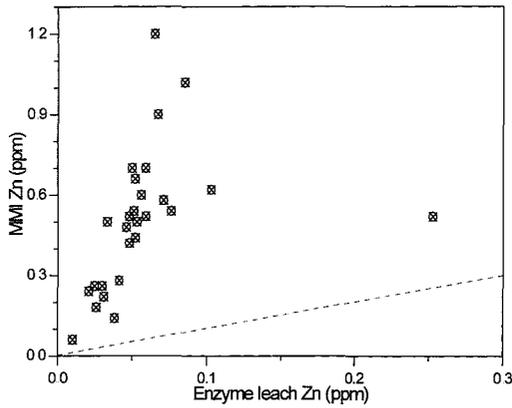


Figure 8: MMI Zn vs Enzyme Leach Zn for Curara samples

**SOIL PROFILE**

Elemental abundances and selective extractions are highly uniform to a depth of 40 cm (results for total Fe and Mn given in Figure 9), with the exception of the uppermost sample (0 - 0.02 m) which has slightly lower contents of total Fe, Sc, Cr, Co, Ba, K, As, REE and Th, possibly because of dilution by recently transported material (e.g., sheet-wash). It also has slightly more Cu and Zn, and more pH 5 acetate-extractable Mn, possibly due to effect of organic matter in the near surface. This uppermost material is generally removed during normal soil sampling, and mass balance calculations (Gray, 1996) indicate that, even if included, this part of the sample would have negligible effect, with the single exception of Mn extracted using pH 5 acetate (Figure 6). This indicates that sampling depth, within the top 40 cm, will not be a critical parameter for selective extraction determinations at this site.

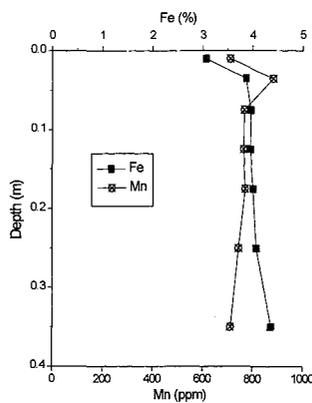


Figure 9: Total Fe and Mn vs depth for soil profile

**INITIAL TRAVERSES (27500N, 27300N AND 25200N)**

The 27500N traverse was originally sampled by CRAE personnel for total and MMI analysis, and the sampling line was repeated, and extended, as part of this project. The original MMI results showed greater Cu, and possibly Cd, concentrations directly above the laterite mineralization, which is at approximately 10 m depth (Figure 10 and Figure 11), whereas the distributions of MMI Zn, Pb, Ni and Ag were not correlated with mineralization (Gray, 1996). For the extractions done in this project, all methods, including total analysis, give anomalous response directly overlying mineralization. No method showed particular superiority in terms of anomaly-to-background, though the worst methods in this respect were pH 5 acetate (high detection limits) and the total concentrations. Specifically, the soils overlying mineralization contain relatively high concentrations of extractable Ba, Be, Cd, Co, Cu, Ni, Pb, REE, U and Zn for most to all of the extractions and for As, Au, Cs, Ga, Hg, Mo, Nb, Sn, Te, Th and Tl for one or some of the extractions. Different techniques were optimal for various elements (e.g., MMI gave the highest contrast for Cu over mineralization, with no enhancement for Co and Ni).

Critically, the best anomaly to background contrast was obtained from extractable Mn (Figure 12), which exceeds 800 ppm total Mn over mineralization, with a background of near zero, whereas amorphous Fe has a maximum of 700 ppm, with a 200 ppm background.

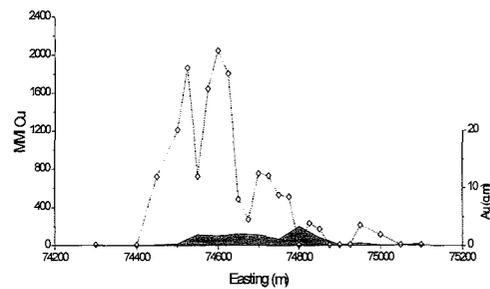
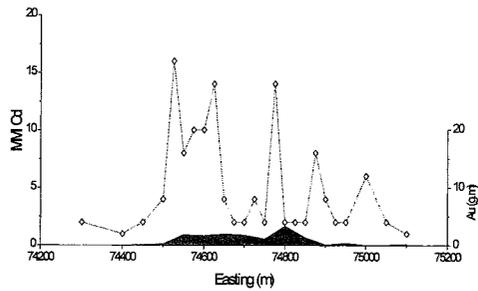
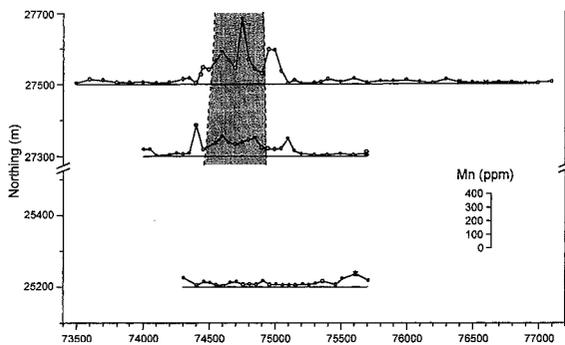


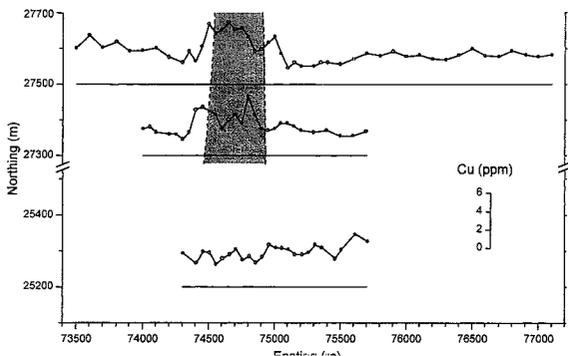
Figure 10: MMI Cu from traverse line 27500N. Shaded area represents Au content of buried laterite.



**Figure 11:** MMI Cd from traverse line 27500N. Shaded area represents Au content of buried laterite



**Figure 12:** Total extractable Mn (by the sequential selective extractions) for traverses 27500N, 27300N and 25200N. Region of buried Au-rich laterite shown in grey.



**Figure 13:** Total extractable Cu (by the sequential selective extractions) for traverses 27500N, 27300N and 25200N. Region of buried Au-rich laterite shown in grey.

The 27300N traverse also overlies mineralization (Figure 2), though it has no clear anomaly observed for the total concentration of any of the elements, except Mn. However, pH 5 acetate Mn and hydroxylamine Fe, Mn, Cu, Zn and Pb (shown for Mn and Cu in Figure 12 and Figure 13) are all enriched above the Au-rich laterite. Thus, extraction results for traverses 27500N and 27300N are correlated with the Au-rich laterite, even where total results are showing poor correlations.

The 25200N traverse is situated in a background area. The results differ from those from the other two traverses in a number of ways:

- i extractable Fe is higher;
- ii extractable Mn (Figure 12) is low and matches the background for the other traverses;
- iii extractable Cu, Zn and Pb (shown for Cu in Figure 13) also lack the enrichments observed from the other traverses.

At first sight, such results would appear to suggest that extraction methods can work effectively even where total concentrations are not giving useful exploration results. However, it was observed that an active (though shallow) drainage system overlies the buried mineralization (Figure 2). Importantly, the soils overlying mineralization (and in the drainage) have high concentrations of separate phase Mn oxides and amorphous Fe. This suggests that the effect of high extractable elements overlying mineralization could be coincidental and related to the surface environment. This was tested by further traverses over drainages in background areas.

#### BACKGROUND DRAINAGE TRAVERSES

The association of extractable metals with either buried mineralization or drainage was tested by additional traverses (the circles in Figure 2), which targeted drainage areas away from mineralization. All samples were extracted by 4 M HCl, which gives good responses and low detection limits, with selected samples extracted by Enzyme Leach and MMI. As shown in Figure 7, and discussed further in Section 4.2, results for 4 M HCl are spatially comparable with MMI and selective extractions. Results for extractable Mn (Figure 14) indicate (with the single exception of a sample from 73400E / 31600N) a clear spatial correlation between extractable Mn and the various drainages in the study area. Other metals showing good correlations with drainage are Ba, Ca, Cd, Co and Ce, and, to a lesser extent, Cu, Ni, Pb, and Zn (Figure 15). Thus, when the entire study area is taken into account, the only clear correlation is between extractable metals and drainage,

and not with mineralization. Plotting extractable elements vs controlling elements (e.g., extractable Mn or Fe) did not indicate any relative enrichment for the mineralized traverse for any of the three tested methods (examples for 4 M HCl extractable Cu and MMI Cd given in Figures 16 and 17, respectively)

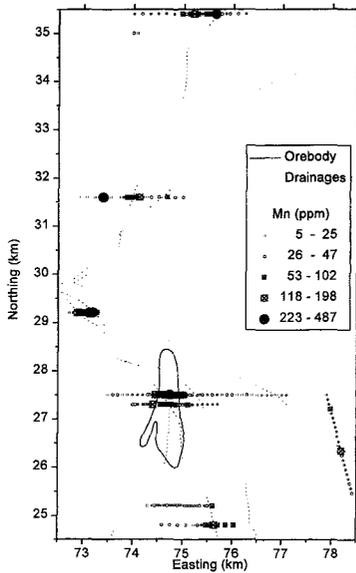


Figure 14: Spatial distribution of 4 M HCl extractable Mn in the Curara district

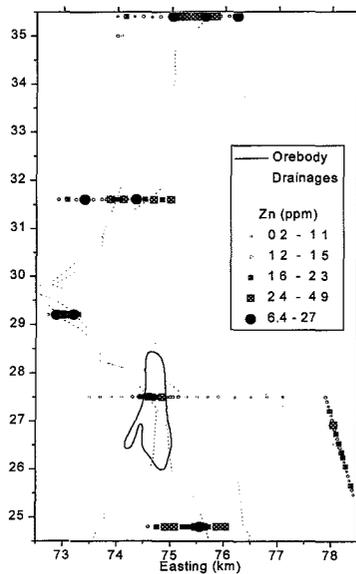


Figure 15: Spatial distribution of 4 M HCl extractable Zn in the Curara district.

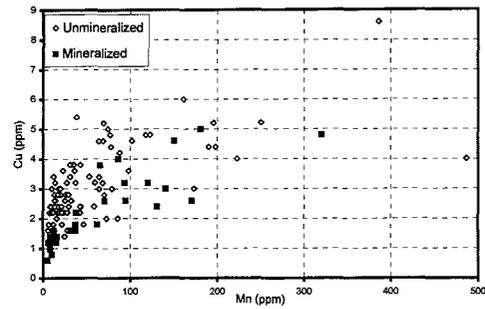


Figure 16: HCl extractable Cu vs HCl extractable Mn for unmineralized and mineralized (27500N) traverses in the Curara district

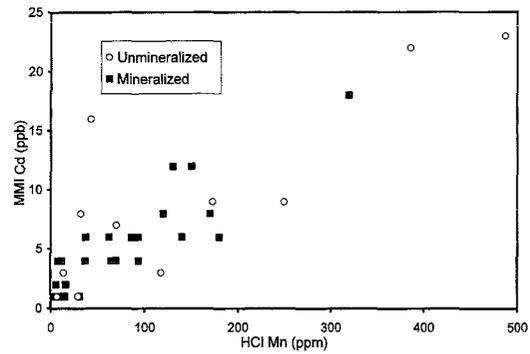


Figure 17: MMI extractable Cu vs HCl extractable Mn for unmineralized and mineralized (27500N) traverses in the Curara district

## DISCUSSION

### FACTORS CONTROLLING EXTRACTABLE TRACE ELEMENT CONTENTS

Curara was chosen as a site where MMI and other selective extraction methods gave soil anomalies that apparently correlated with underlying mineralization. For the initial traverse at 27500N, and for the traverses at 27300N and 25200N (Figure 2), a number of extractions, including MMI, Enzyme Leach, selective extractions and HCl extractions, appeared to show enrichments directly above Au-rich laterite, suggesting that selective and/or partial extractions may well be a potential exploration method at this site. However, the greatest amount of metal dissolved was for Fe (up to 1000 ppm extractable by 0.25 M hydroxylamine and/or 4 M HCl), though this represents only a minor proportion (1 - 2%) of the total Fe. This Fe could be from various amorphous forms (ferrihydrite, Fe in Mn oxides, Fe in other amorphous phases such as allophane) or from surfaces or edges of crystalline Fe oxides (i.e., goethite and hematite). The "best" results, in terms of the magnitude and the signal to noise ratio is Mn, with a clear linear relationship between extractable and total Mn

(Figure 3) Interestingly, extractable Mn and Fe show moderate correlations (Figure 4), even though they are dissolved by different reagents, indicating an secondary cause of these enrichments

Other elements that are enriched above the Au-rich laterite, such as Cd, Cu, Zn and Pb, are primarily correlated with extractable Mn (e.g. Figure 12), even though many of these elements are extracted with the amorphous Fe. However, the metal/Mn ratio actually DECREASES above mineralization, with the greatest reduction for Cu (Figure 13) and the least for Pb (Figure 14). Therefore, the primary effect is NOT an increase in the proportion of extractable trace elements, but an increase in separate phase Mn oxides and, possibly, amorphous Fe above the Au-rich laterite. Indeed, if trace element extraction data are "normalized" by dividing by extractable Mn, the mineralized area shows a negative anomaly.

The results from this site can be directly related to other investigations demonstrating "false anomalies" due to adsorptive phases such as Fe or Mn oxides. For example,

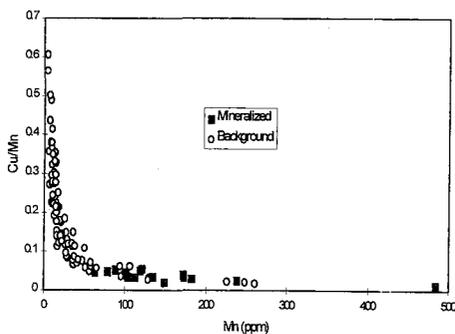


Figure 18: *Cu/Mn vs Mn for hydroxylamine extractions*

Butt and Nichol (1979) showed a relationship between Zn and Mn in stream sediments in Northern Ireland (Figure 19) that is similar to that observed for extraction trace elements at Curara: i.e., for low Mn samples up to a threshold value (in this area 1000 - 2000 ppm) Zn was low (about 50 ppm). For high Mn samples there is an approximately linear relationship between Zn and Mn, with truly anomalous samples in mineralized areas having a higher Zn/Mn ratio than background (Figure 19). NO analogous significant anomaly is observed at Curara (compare Figure 16 with Figure 19). That is, none of the samples at Curara are anomalous for trace metals, the high concentration merely being due to the presence of Mn oxides and/or, possibly, amorphous Fe oxides.

Thus, the initial correlations of extractable metals with the Au-rich laterite are due to a correlation of free Mn oxide with underlying buried Au-rich laterite. Results for

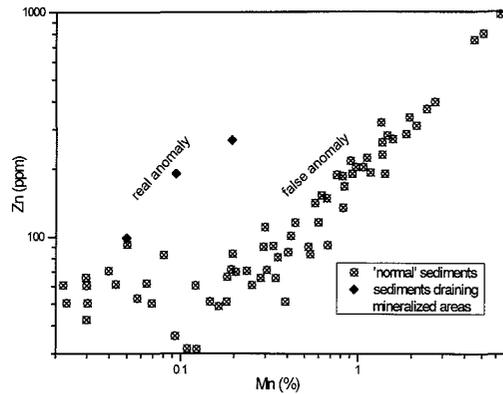


Figure 19: *Zinc and Mn contents of active stream sediments from the Low Sperrins, Co Tyrone, Northern Ireland. Sediments from streams draining mineralized areas show marked deviations from this correlation. (Modified from Butt and Nichol, 1979)*

the entire study area clearly indicate this correlation to be accidental, with the primary correlation being between extractable Mn and surface drainage (Figure 14). This points to the critical requirement for baseline studies to define "true anomalies", based on mineralization, as opposed to anomalies caused by geomorphological factors.

#### HOW DO DIFFERING EXTRACTIONS COMPARE ?

The Curara site was originally selected on the basis of MMI results: MMI Cu and Cd showed enrichments above Au-rich laterite (Figures 10 and 11). These results are closely correlated to extractable Mn (Figure 20), as are these and other elements extracted by all methods. Therefore, whereas for any particular element one extraction may give a better anomaly-to-background contrast than another, all methods are giving similar results, particularly in terms of spatial contrast.

Selection of extraction method should be based on consideration of detection limit vs background, elements of interest and cost:

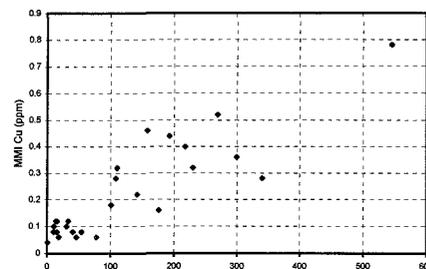


Figure 20: *MMI Cu vs Mn (sum of selective extractions) for Curara.*

- i MMI offers a small suite of elements and does not normally include Fe and Mn;
- ii selective extractions, though giving particular information on the location of elements in phases (in this case carbonates, Mn oxides and amorphous Fe), and therefore useful for initial investigations, give higher detection limits;
- iii Enzyme Leach also had detection limit problems, and possible problems with the high-charge elements;
- iv 4 M HCl gave results comparable with selective extractions, but with better detection limits and was analytically simpler

Therefore, for initial investigations it is recommended that at least some selective extraction analyses are used, so as to test the phase location of elements, whereas for large-scale investigations, the 4 M HCl extraction appears to be the simplest, quickest and most cost-effective method if partial extractions are to be used for exploration. Clearly, the data here is for a single orebody. Similar orientation studies should be conducted across a range of lithologies and target orebodies.

## SUMMARY

At Curara up to 20 m of transported material overlie a lateritic Au resource developed above deep primary mineralization. One shallow profile in the middle of the mineralized zone and eight traverses were tested using selective and partial extraction techniques. The selective extractions, conducted on 3 traverses, involved pH 5 acetate, followed by 0.1 M hydroxylamine, then 0.25 M hydroxylamine. Most of the Mn is dissolved with the 0.1 M hydroxylamine, with Co and (in part) Ba and Ni. Extractable Mn correlates with extractable Fe, even though the Fe is dominantly extracted by 0.25 M hydroxylamine. This indicates an indirect secondary origin for these two phases (e.g., surface drainage depositing Mn and Fe, or biological effects).

The partial extractions used were 4 M HCl (15°C/4 hours), done on 6 traverses, and MMI and Enzyme Leach for one traverse. There was good agreement between the combined results for the selective extractions and the HCl extractions for most elements, despite only a very minor proportion of the total Fe being dissolved, consistent with these extractions dissolving specific Fe-rich components. MMI concentrations were generally lower than for the sequential or HCl extractions, though with similar spatial distribution patterns. The Enzyme Leach concentrations were lower again than MMI.

Soils overlying mineralization contain relatively high concentrations of extractable Ba, Be, Cd, Co, Cu, Ni, Pb, REE, U and Zn for most to all of the extractions and for As, Au, Cs, Ga, Hg, Mo, Nb, Sn, Te, Th and Tl for one or some of the extractions. The best anomaly to background contrast was obtained from extractable Mn, which exceeds 800 ppm over mineralization, with a background of near zero, whereas amorphous Fe has a maximum of 700 ppm, with a 200 ppm background. These two elements appear to be controlling the other element extraction anomalies. The presence of similar anomalies elsewhere in the study area, indicates that this initially hypothesized spatial correlation of extractable (and, weakly, total) metals with the buried Au deposit is coincidental. Surface phenomena, specifically the present-day drainage, are possible causes.

Some of the new extraction techniques currently being introduced for geochemical exploration are partial rather than selective digests: i.e., they extract part of a phase or phases, rather than a selected mineral. They therefore have the potential problem that mineralogical effects (e.g., presence of Mn oxides) may have important effects in the generation of "false anomalies", without information on these effects being available via the extraction results. Therefore, partial extractions such as MMI or Enzyme Leach can only be understood and interpreted correctly if conducted in conjunction with base lines studies, including determinations of critical soil phases such as Mn oxides or other materials expected to adsorb or otherwise accumulate trace elements.

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**REFERENCES**

- Butt, C.R.M. and Nichol, I., 1979 The identification of various types of geochemical stream sediment anomalies in Northern Ireland Journal of Geochemical Exploration, 11: 13-32.
- Butt, C.R.M., Horwitz, R.C. and Mann, A.W., 1977. Uranium occurrences in calcrete and associated sediments in Western Australia Report FP16, CSIRO Australia, Division of Mineralogy, Floreat Park, pp. 67.
- Chao, T.T., 1984 Use of partial extraction techniques in geochemical exploration J Geochem Explor., 20: 101-135
- Clarke, J.R., 1993 Enzyme-induced leaching of B-horizon soils for mineral exploration in areas of glacial overburden Trans Instn Min Metall (Sect B: Appl. Earth sci.), 102:, Jan-Apr 1993
- Gray, D.J., 1996 Selective extraction techniques for the recognition of buried mineralization, Curara Well, Western Australia (CSIRO/AMIRA P409: Weathering Processes Group) CSIRO Division of Exploration and Mining Restricted Report 210R 72 pp.
- Mann, A.W., Gay, L.M., Birrell, R.G., Webster, J.G., Brown, K.L., Mann, A.T., Humphreys, D.B. and Perdrix, J.L., 1995. Mechanism of formation of mobile metal ion anomalies Minerals and Energy Research Institute of Western Australia Report No 153
- Sons of Gwalia Ltd, 1997 Annual Report 1997 ACN 008 994 287