FRACTIONATION OF ZN AND CD IN SOILS PROXIMAL AND DISTAL TO SULPHIDE MINERALISATION.

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INTRODUCTION

In areas with thick transported cover the traditional indicators of bedrock hosted base-metal ore deposits are obscured, and traditional exploration techniques such as drilling are costly and/or ineffective. One solution is to look for other signatures of ore deposits, such as the elevated or depressed concentrations of pathfinder elements (e.g., Zn and Cd) that sometimes occur in soils developed above sulphide ore bodies (e.g., Mann *et al.* 1998). Empirical studies suggest partial chemical extractions improve the detection of these chemical signatures with respect to a bulk soil assay (Mann *et al.* 1998). However, the widespread application of these techniques is hampered by a limited understanding of both the processes involved in creating the chemical signatures (e.g., Smee 1997), and exactly what mineral phase each of these partial extractions removes from the soil (e.g., Hall *et al.* 1996a, b, Hall 1998). In order to address these issues, we aimed to examine if the chemical fractionation of Zn and Cd was different in soils proximal and distal to mineralization, and whether these trends were consistent across semi-arid and wet temperate climatic zones in Australia. Secondly, we investigated which mineral species were targeted by these chemical extractions in our soils.

METHODS

Soils were collected from two climatic zones and mineral belts important to the Australian mineral exploration industry: wet temperate near Queenstown, Tasmania; and, semi-arid near the Elura Pb-Zn-Ag deposit near Cobar NSW. Previous exploration soil surveys (200 m wide transects at 50 m intervals) in both areas defined a zone above mineralization where Cd and Zn concentrations ≤ 10 times the local background. Two samples were collected from each climatic zone: 1) from within the area of increased concentration, referred to as the proximal sample; and, 2) from a site nearby with similar vegetation, topography and underlying geology, but without the increased Zn and Cd referred to as the distal sample. Soils from temperate sites were sampled from the B horizon. Samples from the semi-arid sites were taken from the top 10 cm of the soil profile, where Mann *et al.* (1998) found the maximum concentration of these elements.

Minerals were identified using a combination of Optical Mineralogy (OM), Scanning Electron Microscopy with an Energy Dispersive Spectrometer (SEM/EDS) and X-Ray Diffraction (XRD). OM and SEM/EDS were used to characterize loose and thin-section samples of the soil and XRD was used to characterise the < 2 μm fraction. The concentrations of 53 major, minor and trace elements present within the soils were measured using a combination of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The abundances of mineral and other phases within the soils were visually estimated, and cross-checked against the bulk geochemistry.

The concentrations of Zn, Cd and other elements associated with different fractions of the soil were measured using sequential and selective extractions (Table 1). Fractionation was measured on bulk soil samples as well as three size fractions (< 63 μm, 63-250 μm, > 250 μm). The samples were observed between extraction steps using OM and SEM/EDS to monitor which mineral phases and other materials were attacked.

SAMPLE CHARACTERISTICS

The semi-arid soils were mature and consisted largely of clays, ferruginous concretions and detrital or windblown quartz (Table 2). In contrast, the temperate soils contained high quantities of fresh to slightly weathered lithic fragments. Organic matter was significant only in the temperate proximal soil. All soils were slightly acidic, low in soluble salts (Table 3) and sandy, with approximately 5 and 10% of the temperate and semi-arid samples respectively contained in the < 63 μm fraction.

PARTIAL EXTRACTIONS - SELECTIVITY AND EFFICIENCY

The following results were noted from visual observations of the extracted solutions and SEM investigations of the extracted phases:

- carbonate was no longer observed following the "acid soluble" extraction of the distal semi-arid soil, indicating that this reagent was effective in removing the relatively small amounts of carbonate present in these samples. However, the extracted solution from the temperate soils turned a distinct

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tannin colour, suggesting removal of up to 10 mg/l of carbon (Drever 1997), which equates to > 1.5% of the total organic C present in the distal temperate soil;

- the pyrophosphate extraction dispersed large quantities of colloidal and fine-grained material in all samples studied and prevented filtration prior to analysis. Further, whilst the amount of C removed was less than the detection limit of 0.2%, the reagent extracted up to 0.8% of the Fe, 0.2% of the Mg, 0.3% of the Mn and 0.3 % of the Al present in the soils. Whilst the pyrophosphate extractant has been interpreted to remove ions from organic matter by chelation rather than dissolution (Hall *et al.* 1996a), the amount of material removed from the soil is more than would be expected for the amount of organic matter present, particularly in the semi-arid soils. Observations by SEM indicated effective dispersion of clays and oxides from the quartz particles in the semi-arid soils, and partial dissolution of Mn-rich oxide coatings present in the temperate proximal soil. Thus, it is suggested that whilst this extractant may have removed organically bound ions, it also extracted significant quantities of silicate and oxide based colloids by dispersion, an observation that is supported by Hall *et al.* (1996a); and,
- in the proximal temperate soil the "easily reducible" extraction was largely selective for Mn oxides, with 2,700 ppm of Mn and 0.78 ppm of Fe extracted. However, this extractant did not remove all of the Mn Oxides, as the "reducible" extraction removed a further 8,000 ppm of Mn. The "reducible" extraction was also largely selective for Mn oxides, as less than 200 ppm of Fe and 40 ppm of Al was extracted. Further SEM/EDS observations indicate that Mn-rich oxides were significantly reduced in abundance following the "reducible" extraction, but this was not the case for Fe/Al rich oxides. This result contrasts with previous studies, which found the "reducible" extraction usually targeted amorphous Fe oxides and oxyhydroxides (Hall *et al.* 1996b). Also, despite the high abundance of Fe oxides present in the semi-arid soils, less than 10 ppm of Fe was removed during these extractions combined.

Table 1. Sequential extraction procedures, adapted from Hall *et al.* (1998). Extractions were undertaken on 5 g of soil at 25°C with 50 ml of extractant solution. Deionised water extractions were shaken every half hour for the first two hours. All other extractions were shaken every half hour. * Also conducted as selective extractions.

#	Extraction	Target Fraction	Time	Extractant
1	Highly soluble	Salts	15 hours	Double deionised water
2	Exchangeable	Sorbed ions	2 hours	0.1M $CaCl_2$
3	Acid soluble*	carbonate	5 hours	1 M Na acetate buffered to pH 5 with acetic acid
4	Pyrophosphate extractable *	Organically chelated	7 hours	0.1M sodium pyrophosphate and 0.05 wt% KCN
5	Easily reducible	Mn oxides	2 hours	0.1M hydroxylammonium hydrochloride in 0.01M nitric acid
6	Reducible*	Amorphous Fe Oxides	2 hours	0.25M hydroxylammonium hydrochloride in 0.125M nitric acid
7	Residual	Silicates, Sulphides, Oxides	8 hours	HF/aqua regia

ZN AND CD FRACTIONATION

In the majority of the samples analysed, more Zn and Cd were removed when the extractions were performed on a fresh sample (i.e., during a selective extraction) than when the samples had undergone previous extractions. For Cd this discrepancy is usually very similar to the amount of "exchangeable" Cd present in the samples, suggesting the exchangeable fraction is also removed by the acid, pyrophosphate and reducing extractants. Zn results are similar, although the "acid soluble" extraction consistently removes more than the combined "exchangeable" and "acid soluble" sequential extractions.

Cd was more easily leached in soils from both the semi-arid and temperate regions, with 0-20 % of the total Cd present in the "residual" phase. In contrast, 50-70% of the total Zn was leached during the residual extraction.

The finer grain size fraction generally contained higher concentrations of Zn and Cd than the larger grain sizes and the bulk soil, with increases of generally less than 100% with respect to the bulk soil analyses. It is unlikely that the increased costs of this operation in a mineral exploration environment would be justified by the more favorable detection limits produced.

Temperate soils

The Zn and Cd present in these soils were spread across a number of chemical phases (Table 2, Figure 1).

However, the concentrations of these elements were rarely high enough to enable detection with SEM/EDS in any of the mineral phases identified. Of those that were found to contain high concentrations of Zn, only the Mn Oxides present in the soil proximal to mineralization were abundant enough to constitute a significant source of Zn, and would account for approximately 10% of the total Zn in the sample. High concentrations of Zn were also identified in sulphur containing phases tentatively identified as sphalerite and galena. However, these were present in extremely low abundance and are not considered to be a significant source of either Zn or Cd in these soils.

Zn and Cd were found in similar relative quantities across most of the steps in the sequential extraction scheme, except that there were higher relative concentrations of Zn in the residual and pyrophosphate extractable phases (Figure 1). Also, there appeared to be little difference in the fractionation of these elements between the two soils at this site, apart from the relatively high abundance of "reducible" Cd and Zn in the soil proximal to mineralization. This was most likely due to the lack of Mn oxides in the soil distal to mineralization.

Semi-arid Soils

Zn and Cd were found in a number of phases in the semi-arid site, although they were more restricted than at the temperate locality. SEM/EDS observations suggested that with the exception of the extremely rare carbonates found in the distal soil, none of the phases contained Zn above the detection limit for this technique (ca. 1%). Hand separation and ICP-MS analysis of the ferruginous concretions revealed that these were depleted in both Zn and Cd with respect to the remaining soil matrix in both soils.

In the soil proximal to mineralization at the semi-arid site these elements were released largely during the "exchangeable" and "pyrophosphate extractable" extractions, whereas, the soil distal to mineralization contained almost exclusively "acid soluble" forms of these elements. This is likely due to the lack of carbonate in the proximal soils, which would otherwise lock up Zn and Cd through co-precipitation during wetting and drying events, such is likely to have occurred in the soil distal to mineralization.

EXPLORATION IMPLICATIONS

The partial extraction results confirm previous work indicating that partial extractions are not entirely selective, and do not necessarily remove all of the target phase. This result was particularly prominent when the target was not present in the soil. Therefore, prior to each exploration survey, the components of the soils under study should be assessed and the extractions tailored accordingly.

Both semi-arid and temperate soils had significant differences in the fractionation of Zn and Cd between the soils proximal and distal from mineralization. These include: the presence of a "reducible" fraction of the soil proximal to mineralization at the temperate site, which was distinctly lacking in the soil distal to mineralization; and, the lack of carbonate in the semi-arid soil proximal to mineralization, which appears to contain much of the Zn and Cd in the soil distal to

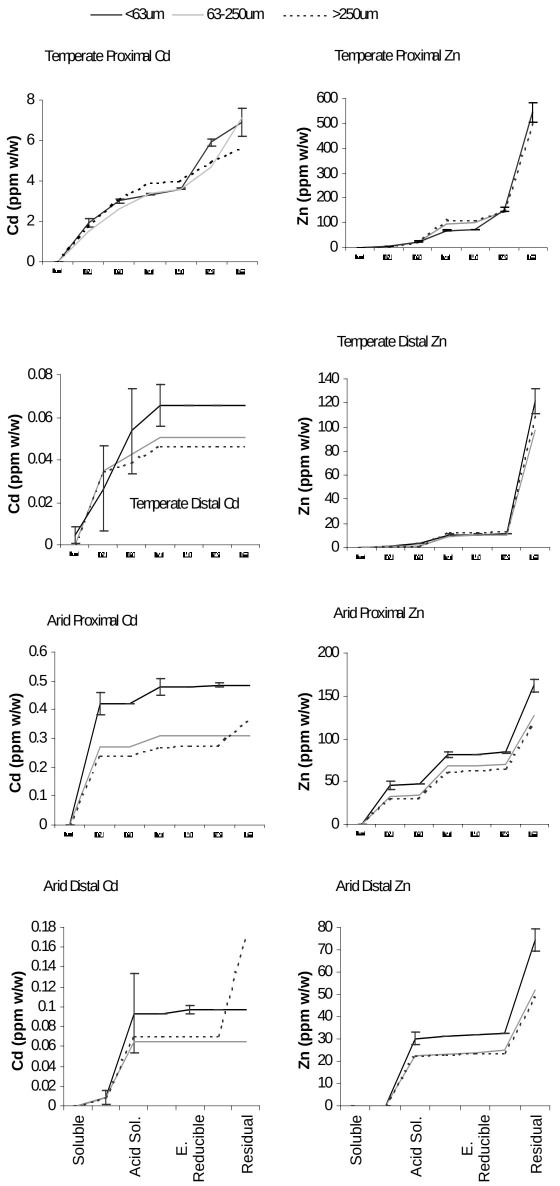

Figure 1: Cumulative concentration of Zn and Cd with each sequential extraction for soils proximal and distal to mineralisation in two climatic zones. Extraction parameters are outlined in Table 1. Error bars represent 1 standard error, and are only shown for the <63 mm fraction to preserve clarity. Errors are similar for the other fractions.

mineralization at the semi-arid site. However, the small number of samples used in this study makes it difficult to determine whether these results are consistent across the zones with elevated Zn and Cd at each site. Further analysis of these fractionation patterns may determine whether these differences are due to the influence of the mineralization at depth or simply local soil variability.

Table 2. Mineralogy and mineral abundance in the (a) Temperate soils, from near Queenstown, Tasmania (b) semi-arid soils, from the Elura Mine, near Cobar, NSW. Results are from a single sample at each site.

(a) Temperate soils	**Size (mm)**	**Proximal Vol %**	**Distal Vol %**	**Zn % w/w**	**Cd % w/w**
Coarse leaf litter[1]	> 20	4	2	<1	<1
Fine organic matter[1,2]	< 2	15	3	<1	<1
Carbonaceous shale fragments[2]	< 2	20	0	<1	<1
Quartz-feldspar porphyry rock fragments [1,2]	0.1 to 0.5	10	10	<1	<1
Volcaniclastic rock fragments [1,2]	0.1 to 0.5	10	60	<1	<1
Mn poor Fe/Al oxide coatings	Variable	~1	<1	<1	<1
Mn rich Fe/Al oxide coatings	Variable	~1	<1	~2	<1
Pyrite [2,4]	< 0.05	<1	<1	<1	<1
Galena, Chalcopyrite, Sphalerite [4]	< 0.05	<<1	<<1	<1-20	<1
Fine grained mix (<2μm) of muscovite, clays and quartz, ± rutile, K-feldspar [2,3,4]	< 0.05	40	25	<1	<1

(b)semi-arid soils	**Size (mm)**	**Proximal Vol %**	**Distal Vol %**	**Zn % w/w**	**Cd % w/w**
Coarse organic matter [1,2]	Variable	2	2	<1	<1
Fractured, poorly sorted plutonic quartz [2]	Variable	5	8	<1	<1
Possibly windblown, mostly volcanic quartz [2]	~0.1	10	15	<1	<1
Carbonate [4]	<0.05	Not obs.	<1	~2	<1
Iron pisoids and iron-rich lithic fragments [1,2,4]	2-50	30	5	0.006 ^{p} 0.0015 ^{d}	0.0003 $^{p\,d}$
Fine grained mix (<2μm) of muscovite, clay and quartz [2,3]	<0.05	53	70	0.03 ^{p} 0.004 ^{d}	0.0007 $^{p\,d}$

Mineral identification method: [1]Hand specimen, [2]Binocular Microscope, [3]X-Ray Diffraction, [4]SEM, in conjunction with EDS. Zn and Cd contents with ^{p} and ^{d} are derived from hand separated fractions from the soils proximal and distal to mineralisation respectively, and analysed by ICP-MS. All other contents are derived from EDS measurements, and are semi quantitative with a detection limit of approximately 1%.

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Table 3. Basic chemical parameters. EC and pH were analysed on a 1:5 extract with deionised water. The high concentration of carbon in the proximal temperate soil was influenced by the presence of bedrock derived carbonaceous (black) shale fragments.

	Proximal semi-arid	**Distal semi-arid**	**Proximal Temperate**	**Distal Temperate**
pH	5.2	5.2	5.9	4.8
EC (μS)	82	100	150	57
Total Carbon (% w/w)	1	1	17	3

REFERENCES

DREVER J.I. 1997. *The Geochemistry of Natural Waters*. Prentice Hall, 436 pp.

HALL G.E.M., VAIVE J. & MACLAURIN A. 1996a. Analytical aspects of the application of sodium pyrophosphate reagent in the specific extraction of the labile organic component of humus and soils. *Journal of Geochemical Exploration* **56,** 23-36.

HALL G.E.M., VAIVE J., BEER R. & HOASHI M. 1996b, Selective leaches revisited, with emphasis on the amorphous Fe oxyhydroxide phase extraction. *Journal of Geochemical Exploration* **61**, 59-78.

HALL G.E.M. 1998. Analytical perspective on trace element species of interest in exploration. *Journal of Geochemical Exploration* **61,** 1-19.

MANN A.W., BIRRELL R.D., MANN A.T., HUMPHREYS D.B. & PEDRIX J.L. 1998. Application of the mobile metal ion technique to routine geochemical exploration. *Journal of Geochemical Exploration* **61**, 87-102.

SMEE B.W. 1997. The formation of surficial geochemical patterns over buried epithermal gold deposits in desert environments: results of a test of partial extraction techniques. *In:* Gubins A. ed. *Proceedings of Exploration 97: Fourth Decennial international conference on mineral exploration*, 301-314.