WEATHERING-CONTROLLED FRACTIONATION OF ORE AND PATHFINDER ELEMENTS PART II: THE LAG STORY UNFOLDS

Kenneth G. McQueen[1], Dougal C. Munro[2], David Gray[3] & Maite Le Gleuher[1]

[1]CRC LEME, Department of Earth and Marine Sciences, Australian National University, ACT, 0200
[2]Cobar Management Pty Ltd, CSA Mine, Cobar, NSW, 2835
[3]CRC LEME, CSIRO Exploration and Mining, Bentley, WA, 6102

INTRODUCTION

Surficial lag is widespread in many deeply weathered terrains in arid and semi-arid environments. This lag generally consists of the most chemically and physically resistant components of the regolith and is typically dominated by quartz, quartz-rich lithologies and ferruginised materials. It has been widely used as a sampling medium in geochemical exploration (generally the 3-15 mm size fraction) on the assumption that it retains ore and pathfinder elements present in the underlying bedrock.

Previous studies of the weathering zones over polymetallic sulfide mineralisation in the Cobar area have shown that ore-related elements are partitioned to particular secondary host minerals as a result of prolonged and complex chemical weathering (e.g., Cairns *et al.* 2001, McQueen & Munro 2003, 2004, Leverett *et al.* 2003, 2004). In the upper, oxidised part of the profile stable iron oxides/oxyhydroxides (particularly goethite and hematite) become important repositories for many of these elements. As these minerals are exposed at the surface they undergo further chemical and physical transformations and (with their contained trace elements) can also become widely dispersed across the landscape by mechanical erosion processes. Previous work on the bulk chemistry of different lag components has indicated that there is a significant fractionation of trace elements during this lag maturation and transport (McQueen & Munro 2003). The precise nature and control on this fractionation is the subject of further investigation and the results of the first stages of this work are presented here.

PHYSICAL AND CHEMICAL MATURATION OF LAG

Lag accumulates at the surface by a number of processes including surface deflation, bioturbation and differential movement related to shrink-swell of clays and soil creep (Figure 1). Chemically stable and residual components exposed at the surface are further concentrated as a result of winnowing, or removal of the finer and lighter material by sheetwash and wind. Lag concentration is greater in areas of lower relief where normal surface runoff is unable to remove the coarser or more dense fractions.

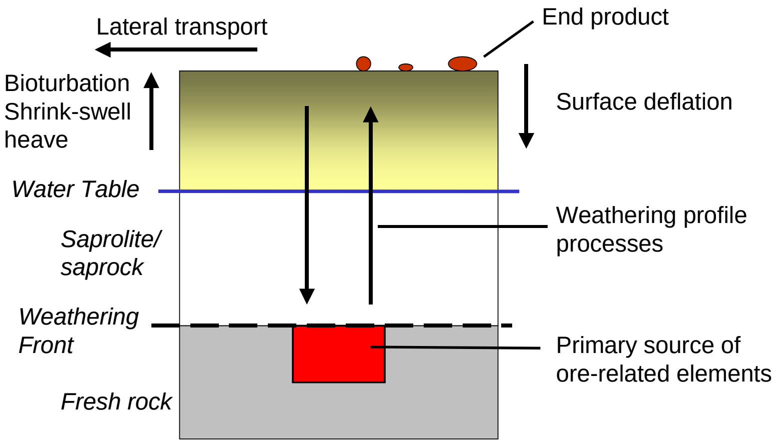


Figure 1: Schematic summary of processes involved in the formation of lag. Residual weathering products concentrate as surface lag and can retain ore-related elements from the primary source.

Lag is subject to mechanical reworking, transport and further chemical change, which result in physical and chemical maturation (Figure 2). Abrasion by sheetwash and fluvial reworking leads to progressive decrease in grainsize and increase in rounding of the lag. Chemical changes involve conversion of residual goethite to hematite and formation of varying amounts of maghemite. Loss of the soluble components and precipitation of additional hematite, typically on outer surfaces (as concentric cutans) or infilling fractures and pore spaces, results in a progressive increase in the Fe and hematite content of the lag. Biological processes may also be involved in these surface transformations.

In: Roach I.C. ed. 2004. *Regolith 2004*. CRC LEME, pp. 241-246.

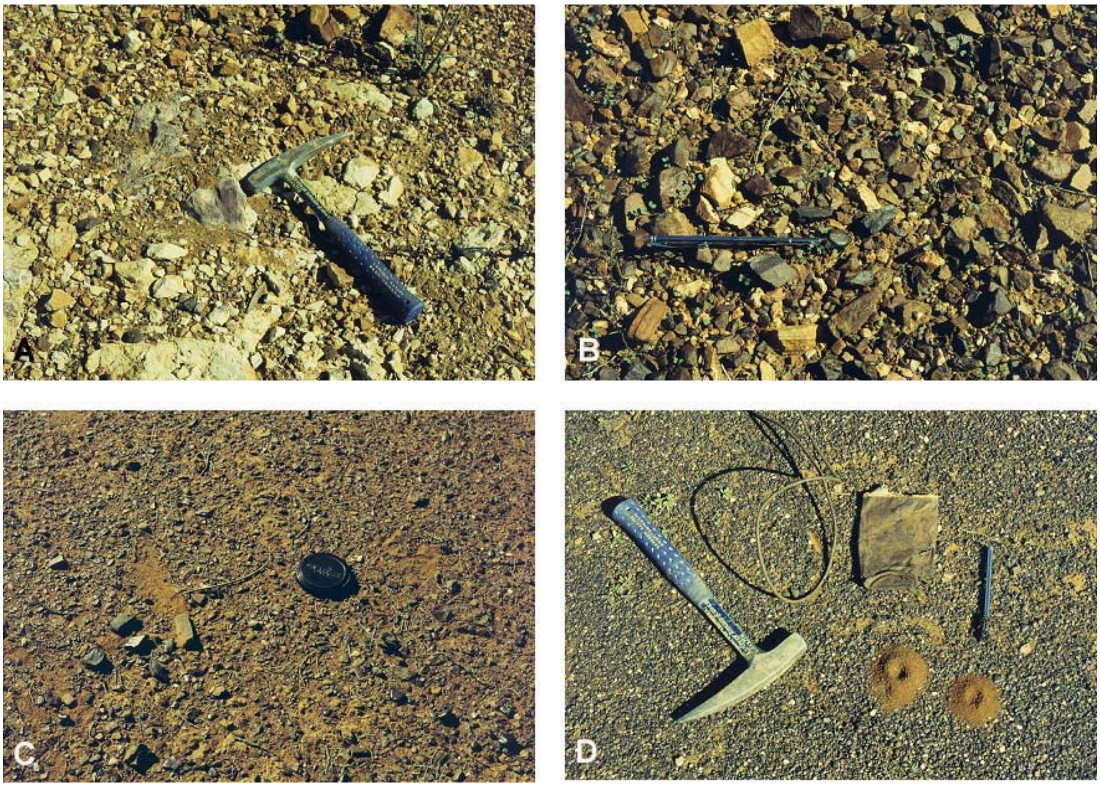


Figure 2: The transformation of lag related to surface physical and chemical maturation. **A**. Saprolite/saprock and ferruginous mottles exposed by surface erosion/deflation. **B**. *In situ* lag from an erosional rise, composed largely of coarse and angular quartz, lithic and ferruginised lithic components, with some highly ferruginous lag. **C**. Lag from a colluvial plain, composed dominantly of reworked and transported ferruginous components with minor coarse and angular fragments. **D**. Highly ferruginous, pisoidal lag from an alluvial flat showing a high degree of physical and chemical maturation (various items for scale),

Previous work on lag from ten sites in the Cobar-Yarrawonga area (McQueen & Munro 2003) revealed a strong positive correlation between Fe (and also hematite) content of lag and some trace elements, including Th, Hf, Pb, As, Sb, Bi, Ba and Cr. The abundances of these elements and Fe also increase systematically with degree of rounding or physical maturation of the lag. Other elements (including Cu and Zn) do not show this relationship and in some cases are negatively correlated with Fe and hematite content. As these samples were from sites with possible anomalous concentrations of ore and pathfinder elements, we have examined samples from four additional sites: one (background) site, well removed from any known mineralization; and three sites from an area of known mineralization, including one close to an eroding Pb-Zn gossan near the CSA mine, just north of Cobar.

Bulk geochemical analyses of different lag fractions from the background site confirm a strong positive correlation between Fe and elements such as Th, Pb, As, Sb and Bi. They also reveal a general negative correlation for Cu and Zn. This trend also shows a systematic pattern of increasing Fe and correlated element content with degree of rounding or physical maturation of the lag (Figure 3). The fractionation trends for the various elements are very similar to those found previously for most of the samples from the Yarrawonga lag anomaly. This suggests that the elevated levels of pathfinder elements in some of the Yarrawonga samples could be the result of chemical transformations that have increased their concentrations from background levels. Thus anomalous levels of As, Pb, Sb and Bi may not be indicative of nearby mineralization.

Lag samples from the CSA area show similar trends for those elements positively correlated with Fe and hematite, but the ratios against Fe are higher for target and pathfinder elements associated with the known mineralisation in the area. Thorium shows a very similar ratio to that found at Yarrawonga and the background site. Different lag fractions from the sample collected near the outcropping Pb-Zn gossan show markedly different trends (Figure 4).

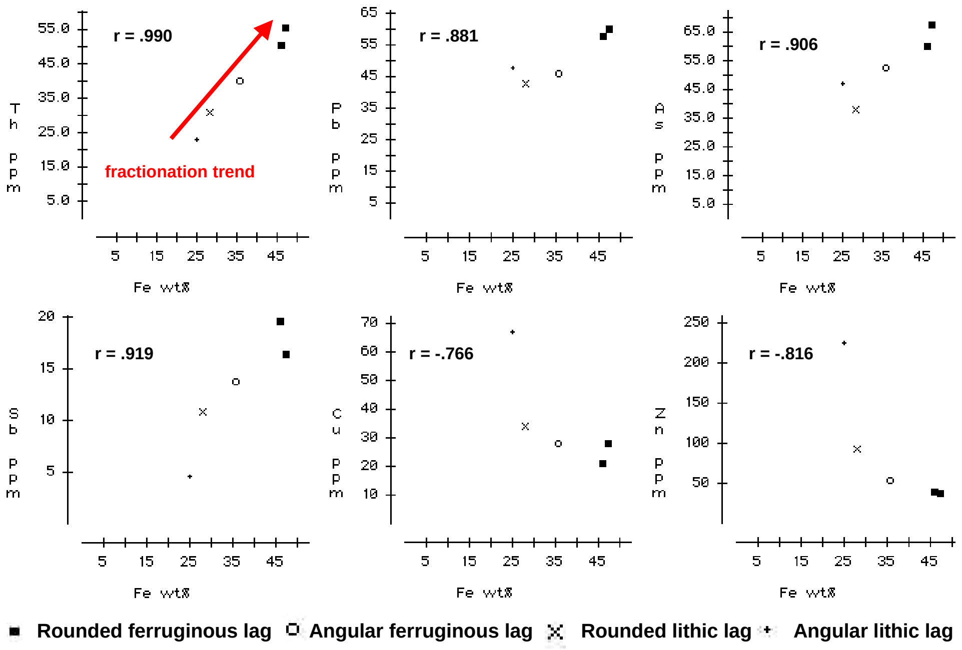


Figure 3: Bivariate plots of some trace elements versus Fe for different lag fractions from a background lag site developed over weathered distal turbidites of the Amphitheatre Group, 40 km south of Cobar (r = correlation coefficient). Bulk sample analysis was by INAA and ICP OES.

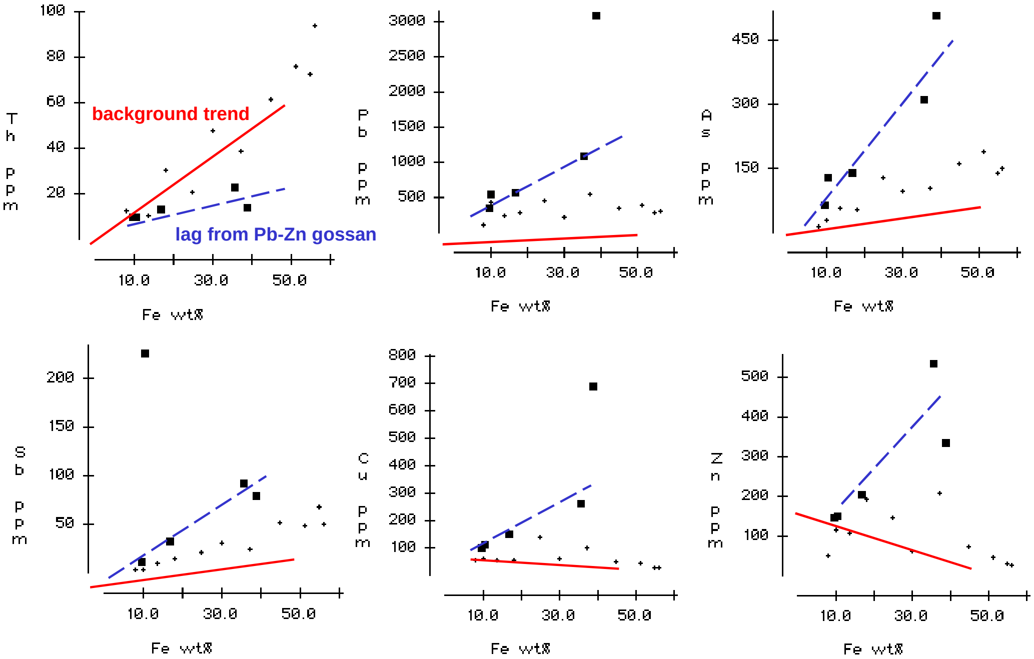
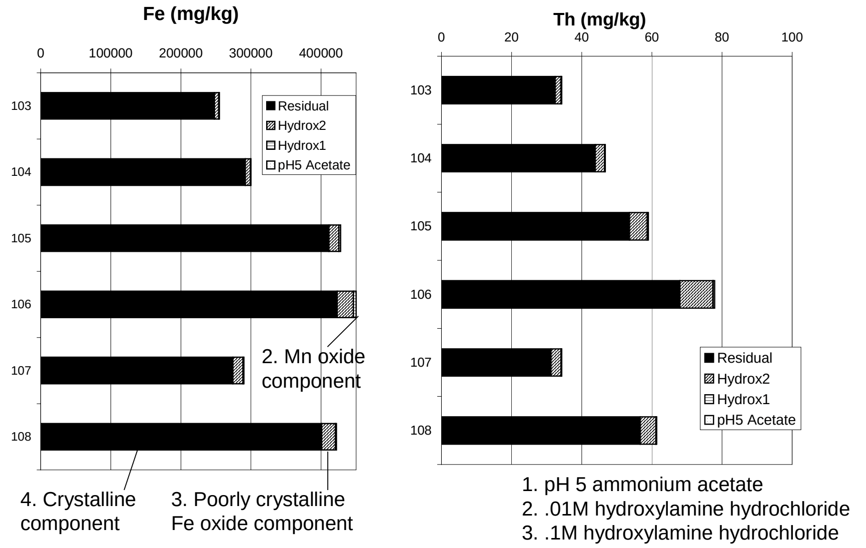


Figure 4: Bivariate plots of trace elements versus Fe for different lag fractions in three samples derived from and area of known Pb-Zn mineralisation around the CSA mine, Cobar (small points). Also shown are plots for different lag fractions for a sample collected near an outcropping Pb-Zn gossan (squares). Bulk sample analysis was by INAA and ICP OES.

CONTROLS ON ELEMENT DISTRIBUTIONS

Two approaches have been taken to further investigate the mineralogical controls on the observed patterns of element distribution in lag. These include sequential leach analysis and *in situ* analysis at the micro scale.



1. pH 5 ammonium acetate
2. .01M hydroxylamine hydrochloride
3. .1M hydroxylamine hydrochloride
4. residual from total analysis by INAA

Figure 5: Results of sequential leach analysis of different lag fractions for Sample 1 from Yarrawonga. 103 is angular ferruginised lithic lag, 104 is rounded ferruginised lithic lag, 105 is angular hematite-rich lag, 106 is rounded hematite-rich lag, 107 is angular magnetic ferruginous lag, 108 is rounded magnetic ferruginous lag. Leachant 1 removes loosely bound ions, leachant 2 dissolves the manganese oxide component and leachant 3 dissolves the poorly crystalline iron oxide component. The residual is considered to be tightly bound or in the crystalline component of the lag.

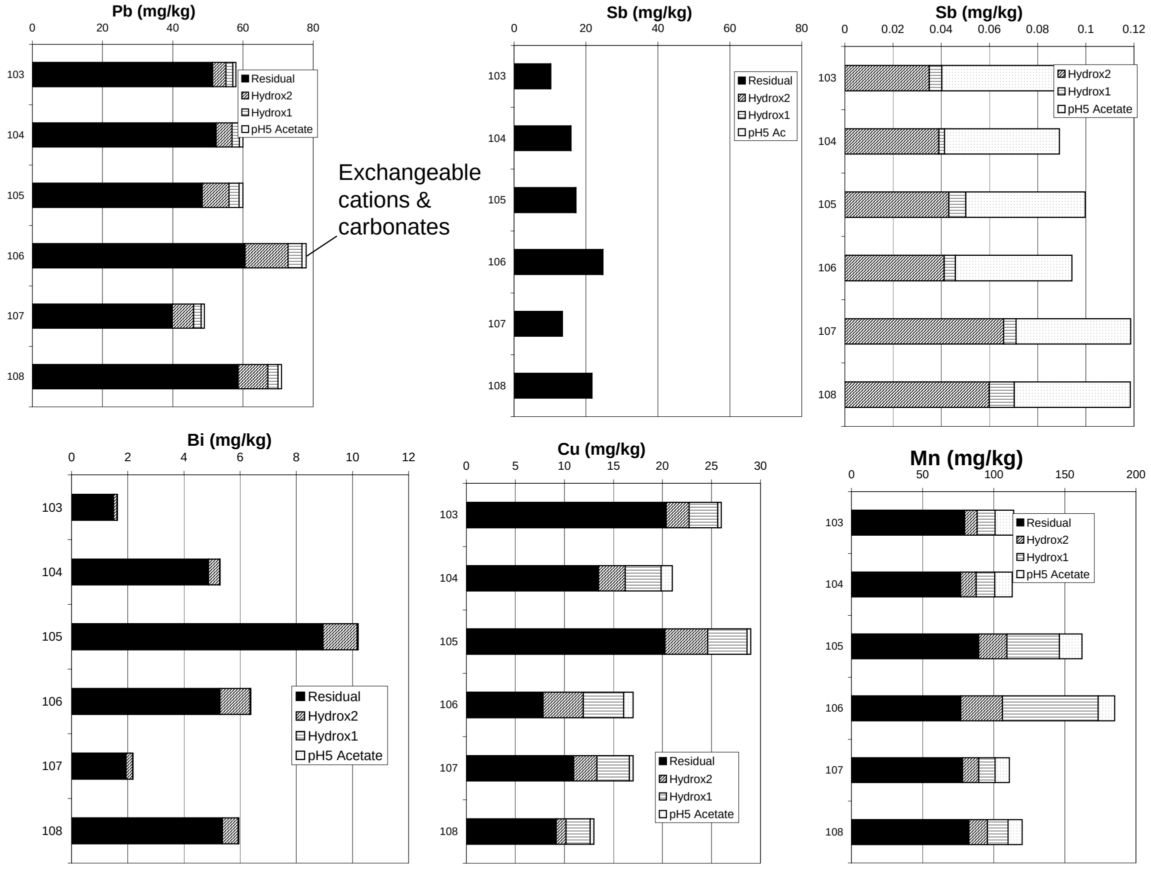


Figure 6: Results of sequential leach analysis of different lag fractions for Sample 1 from Yarrawonga for some additional elements. Lag fractions and leachants are the same as for Figure 5. The upper part of the Sb plot has been expanded to show the very small amounts present in the non-residual components.

Sequential leach analysis involved treating the powdered samples with a series of leachants that selectively removed loosely bound exchangeable cations, then dissolved the manganese oxide component of the sample and finally attacked the poorly crystalline iron oxides. The leachants used were pH 5 ammonium acetate, 0.01M hydroxylamine hydrochloride and 0.1M hydroxylamine hydrochloride respectively (see Chao 1984). Derived solutions were analysed using ICP-MS. The sequential leach approach is subject to some uncertainties related to leach times and particle size, but it should give a broad guide to the distribution of elements in different components of the lag. Results for one sample site are shown in Figures 5 and 6, and indicate that for Fe, Th, Pb, Sb and Bi only a very small proportion of the elements are loosely bound or in exchangeable form. Very small proportions of Fe, Th, Sb and Bi are present in the manganese oxide component, but a larger proportion of the Pb is present in this form. Significant, but still small, proportions of all these elements appear to be present in the poorly crystalline iron oxide component. Barium and S (not shown in Figure 6) have more than half their content present in the loosely bound form and most of the remainder in the residual component. The major proportions of the Fe-correlated elements (except for Ba) in all the lag fractions appear to be strongly bound within the crystalline component of the lag. This is not surprising given that the lag has been exposed at the surface for long periods of time with ample opportunity for loosely bound elements to be removed or incorporated into more crystalline forms. The proportions of the elements reporting to the different components are roughly similar for the different lag fractions. Copper, which is one of the elements not strongly correlated with Fe and hematite content, is present in much greater proportion in all the non-residual components. Manganese is also significantly present in manganese oxides and exchangeable forms. The overall Mn content of the lag is low (< 250 ppm), which may explain the low amounts of elements indicated as hosted by manganese oxides. These results are similar to sequential leach analyses reported for less mature lag samples collected over two mineralised sites in the Cobar Goldfield (Cairns *et al*. 2001).

Initial investigation of trace element distributions using Scanning Electron Microscopy (SEM) and Electron Microprobe Analysis (EMP) on a small number of lag samples has not yet proved fruitful, largely due to the insufficient detection limits of the electron microprobe. The maximum Pb, As, Sb, Bi and Th contents of the different lag fractions from the background and Yarrawonga sites are 90, 80, 280, 25 and 55 ppm respectively and if these elements are distributed throughout the hematite component (rather than in separate enriched phases) they would not be detected by normal EMP analysis. Some areas of high S content were detected during the probe analysis, indicating the presence of sulfate minerals in some lag samples. These areas did not have detectable levels of the trace metals.

Follow-up, detailed SEM work is planned as well as EMP analysis of samples with higher trace element contents from the CSA area. It is also planned to examine a suite of samples by laser ablation ICP-MS, a technique that has much lower detection limits although less spatial resolution.

DISCUSSION

Work to date has shown that certain trace elements including As, Bi, Cr, Hf, Pb, Sb and Th are concentrated with Fe and hematite in lag as it undergoes physical and chemical maturation under surface conditions. These elements are largely bound in the crystalline component of the lag and appear to be contained within hematite. However, it seems unlikely that they could substitute directly for Fe in the hematite structure, given their ionic charge and radius characteristics. Antimony could possibly substitute in hematite as $Fe_{0.67}\,Sb_{0.03}O_3$ (A. Christie *pers. comm*. 2004). The trace elements could occur within microscopic inclusions of separate minerals in the hematite, but at this stage they appear to show a very even distribution through the hematite in the lag. Possible candidates for separate mineral hosts include minerals with similar crystallographic or chemical parameters to hematite, for example members of the crichtonite group ($(Pb,Sr,Ba,Th,U,Y)(Fe^{3+},Ti,Cr,V)_{21}O_{38}$) or magnetoplumbite ($Pb(Fe^{3+},Mn^{3+})_{12}O_{19}$).or magnetoplumbite. Phosphorous contents are elevated in some of the high Pb lag fractions from the CSA area suggesting the possibility of plumbogummite ($PbAl_3(PO_4)_2(OH)_5.H_2O$) as a host phase for Pb in these samples. The P content is typically lower, or not correlated with Pb, in the background and Yarrawonga lag samples. Small areas of high S content detected by EMP analysis in some lag samples, suggest the possible presence of alunite-jarosite group minerals. The bulk S content of all the lag fractions from all sample sites ranges from 60 to 780 ppm. Elevated S associated with high Ba contents in some samples suggests the possible presence of barite as a host phase for Ba. A high proportion of Ba and S are in loosely bound form in the lag fractions subjected to sequential leach and it is not clear why this should be.

The concentration of Th with increasing maturation of the lag is particularly interesting. Its strong positive correlation with Fe and hematite content suggests it is hosted in hematite. Thorium shows strong negative correlations with P, Ce, La and Zr indicating that its abundance is not reflecting residual monazite or zircon.

The relationship between Th and Fe provides a useful indicator of weathering-related chemical fractionation of ferruginous lag. The Th content can also be used as a measure of the hematite content and degree of physical maturation or reworking/transport of the lag. Based on this finding, detailed analysis of the Th channel in airborne radiometric imagery may provide a tool for mapping areas of transported versus *in situ* ferruginous lag.

The fractionation of some pathfinder and ore-related elements with lag maturation has implications for interpreting lag geochemistry, particularly where the lag samples contain variable mixtures of the different lag fractions. Lag data should be normalised for Fe content for those elements that concentrate with hematite (As, Pb, Sb, Bi) but not for those that are independent of hematite content (Cu, Zn). This can reduce the geochemical noise related to varying hematite abundance. Typical background trends for elements against Fe can be recognised. Data from the CSA sites indicate that lag in this mineralised area has higher ratios of ore-related elements over Fe and also that lag derived from a Pb-Zn gossan shows very distinct trends. This indicates the possibility of constructing templates for background ratio trends, which can then be used to isolate and detect truly anomalous values.

CONCLUSIONS

Further work is required to fully understand the mechanisms of trace element fractionation in ferruginous lag and to establish the exact host sites for the elements involved. Knowledge acquired to date indicates the general nature of the process and the importance of taking fractionation into account when interpreting lag geochemistry involving fractionated elements (e.g., As, Pb, Sb, Bi), particularly for samples containing variable mixtures of lag with different degrees of maturity. It is possible to construct templates for background fractionation trends, which can be used to isolate truly anomalous values. These templates should be particularly valuable for isolating subtle lag geochemical anomalies. The findings also highlight the importance of knowing the regolith-landform setting and history of transport of the lag collected in lag sampling programs.

Acknowledgments: The work reported here was supported by the Australian Government's Cooperative Research Centre Program, within CRC LEME. The study was encouraged and supported by Peak Gold Mines Pty Ltd and Cobar Management Pty Ltd.. Geochemical analyses were performed by Becquerel Laboratories, Lucas Heights, and Genalysis (Perth). Andy Christie (CRC LEME, ANU) provided some useful comments on potential mineral hosts for trace elements.

REFERENCES

CAIRNS C.J., MCQUEEN K.G. & LEAH P.A. 2001. Mineralogical controls on element dispersion in regolith over two mineralised shear zones near the Peak, Cobar, New South Wales. *Journal of Geochemical Exploration* **72**, 1-21.

CHAO T.T. 1984. Use of partial extraction techniques in geochemical exploration. *Journal of Geochemical Exploration* **20**, 101-135.

LEVERETT P., MCKINNON A. R. & WILLIAMS P.A. 2003. Mineralogy of the oxidised zone at the New Cobar orebody. *In:* ROACH I.C. ed. *Advances in Regolith*. CRC LEME, pp. 267-270.

LEVERRETT P., MCKINNON A.R. & WILLIAMS P.A. 2004. A supergene model for Cobar style deposits. *In:* MCQUEEN K.G. & SCOTT K.M. eds. *Exploration Field Workshop Cobar Region 2004*. CRC LEME, pp. 46-50.

MCQUEEN K.G. & MUNRO D.C. 2003. Weathering-controlled fractionation of ore and pathfinder elements at Cobar, NSW. *In:* ROACH I.C. ed. *Advances in Regolith.* CRC LEME, pp. 296-300.

MCQUEEN K.G. & MUNRO D.C. 2004. Factoring in weathering-controlled chemical fractionation in suface sampling media. *In:* MCQUEEN K.G. & SCOTT K.M. eds. *Exploration Field Workshop Cobar Region 2004.* CRC LEME, pp. 57-61.