BIOGEOCHEMICAL SAMPLING MEDIA FOR REGIONAL- TO PROSPECT-SCALE MINERAL EXPLORATION IN REGOLITH-DOMINATED TERRAINS OF THE CURNAMONA PROVINCE AND ADJACENT AREAS IN WESTERN NSW AND EASTERN SA

S.M. Hill

CRC LEME, School of Earth and Environmental Sciences, University of Adelaide, SA, 5005

INTRODUCTION

In recent years a range of regolith biogeochemistry research projects have been undertaken in the Curnamona Province and immediately adjacent areas in western New South Wales and eastern South Australia. The biogeochemistry of tree and shrub species, as summarised in Hill & Hill (2003), has been the main focus of the research, although increasing consideration is being given to faunal biogeochemical characteristics. This manuscript provides a brief overview of some of the highlights of this research program.

RESEARCH STRATEGY

The ultimate aim of the research program has been to develop the application of biogeochemical sampling media for use in mineral exploration and environmental chemistry sampling programs. There is more to this than simply picking parts of plants and sending them off to the laboratory for analysis. Biogeochemical sampling media are typically dynamic and complex, however, by having some respect for the characteristics of the media to be sampled a suitable sampling strategy can be developed. The sampling strategy needs to be rigorous and robust, with a major aim being the collection of consistent and therefore comparable sampling media. Once the sampling and then the sample preparation and assay technique have been decided upon the assays generated can be used for establishing knowledge of the biogeochemical characteristics and then interpretations of biogeochemical mechanisms and controlling factors. These are important because they are major aspects of biogeochemical dispersion and residence models, which ultimately determine the type of application that particular biogeochemical media can be used for, and how the assay results will be interpreted. This biogeochemical research strategy towards the application of these materials as a sampling media has followed the paths shown within the flowchart in Figure 1.

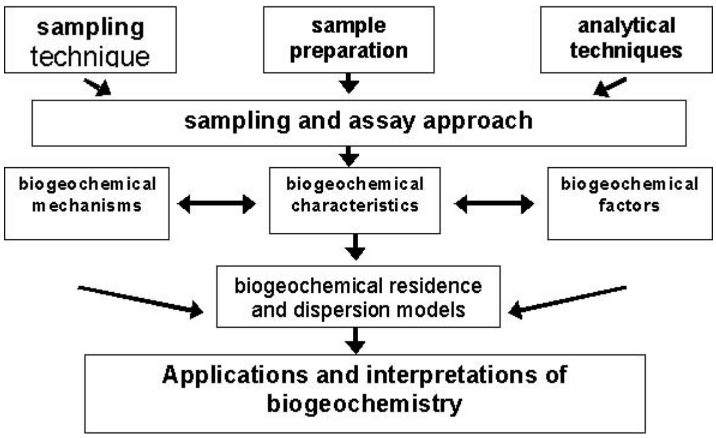

Figure 1: Biogeochemistry research and applications flow chart.

One way to consider the array of biogeochemical sampling media available in most landscapes is that once characterised and understood, each medium can be seen as a sampling and chemical processing tool within the larger biogeochemical toolbox of the landscape.

Some media will be best used for regional sampling programs. These will typically have a widespread distribution across large geographical areas and either occur within a range of regolith-landform settings or within a widespread regolith-landform setting which is of regional significance (e.g., along major drainage channels). They will also derive their biogeochemical signatures from broad areas (dispersion pathways of 100s to 1000 metres), either through amalgamation of the chemistry from a large area (such as extensive root systems) or else from a substrate that is an amalgamation of regional chemical signatures (e.g., stream sediments or particularly fine-grained overbank deposits). These attributes produce regional sampling media that derive their biogeochemical signatures from broad areas and can be sampled on relatively large sample spacing to efficiently account for large regions. Examples of regional sampling media developed by this research program include regional river red gum sampling and macropod (red and western grey kangaroo) scat sampling.

Other media are best suited to local-scale, detailed sampling programs. They are typically sensitive to local substrate chemical changes (e.g., plants with restricted root systems), and are best sampled at relatively close

In: Roach I.C. ed. 2004. *Regolith 2004*. CRC LEME, pp. 128-133.

sample spacings. It is recommended that these media be used to refine and further constrain interesting regional sampling media results, rather than being used for regional scale sampling programs, because they are associated with dispersion pathways operating on the scale of metres to 10s of metres. Plants used in this way may have root systems restricted to either mostly vertical penetration of the regolith to the underlying bedrock or aquifer systems, or else have root systems that amalgamate chemical signatures from locally derived regolith materials. Examples of locally applicable sampling media include prickly wattles (*Acacia victoriae*), mulga (*Acacia aneura*), and chenopod shrubs (e.g., *Maireana spp.* and *Atriplex spp.*).

SAMPLING AND ASSAY APPROACH

The early stages of this research program have focussed on establishing a robust and rigorous sampling strategy. This included extensive reading and review of previous literature as well as the trial of different approaches specific to both the particular indigenous flora being sampled, and the specific goals of particular sampling programs. Many of the details of this stage of project development are outlined in L. Hill (2002), with more recent accounts specific to particular species such as river red gums (*Eucalyptus camaldulensis*) (Hulme & Hill 2003, 2004). Sample preparation approaches adopted are outlined and discussed in L. Hill (2002, 2003) and Hulme & Hill (2003). One component that has been found to be extremely important as a framework for conducting and then interpreting biogeochemical surveys is the provision of a suitable regolith-landform map. Regolith-landform setting is a major control on the biogeochemical assay results (e.g., Hill 1995, Brown & Hill 2003, 2004). The regolith-landform maps used need to have meaningful descriptions and subdivision of the regolith-landform units as well as the potential to show dispersion pathways, and hopefully some vegetation community and dominant species information (S. Hill 2002, Brown & Hill 2003).

BIOGEOCHEMICAL CHARACTERISTICS

In order to establish some of the chemical parameters specific to individual biogeochemical sampling media, sampling studies have been undertaken in both 'background' and 'extreme' chemical landscape settings. These 'extreme' settings have included sites overlying or proximal to mineralisation (e.g., Jones 1999, Debenham 2000, Senior 2000, Dann 2001, Hill & Hill 2003, Hulme & Hill 2003, Brown & Hill 2004), or bedrock types with extreme rock chemical compositions such as serpentinites and other ultramafic rocks (Hill 1998, Hill & Hill 2003, Barratt & Hill 2003). An summary of some of the 'extreme' assay results from trees sampled near the Junction Mine on the Broken Hill Line of Lode are given in Table 1. For the biogeochemical sampling media and elements listed here, when at 'background' many of the elements (e.g., Ag, Pb, Cd, Sb) are typically in concentrations below the detection limits of the assay techniques, or in the case of Zn, are typically in concentrations of 10s of ppm rather than the elevated figures shown here.

Determining meaningful Au assays of many biogeochemical media has been a major challenge for characterisation in areas prospective for Au, such as Tibooburra and the Williams Peak Prospect near Kayrunnera. Firstly, many media assayed for Au also have high Na contents, which interfere with obtaining INAA Au assays at low detection limits. This was a major problem for bladder saltbush (*Atriplex vesicaria*) and many other chenopod leaf assays where the plant leaf contains salt secretion glands, and has been overcome by preferentially sampling the twigs from these shrubs (Brown & Hill 2004). The Au content also appears to be extremely heterogeneous and seasonally variable within many plants, such as river red gums (Hulme & Hill 2003, 2004), and large robust sampling approaches within optimal seasonal conditions

Table 1: Biogeochemical assay ranges for various trees and shrubs sampled from over or adjacent to the Broken Hill Line of Lode, near Brownes Shaft (Junction Mine).

Species/organ (n = sample pop.)	Elements	Assay Technique*	Assay Range
Eucalyptus camaldulensis	Ag	INAA	< 0.1 – 0.23 ppm
Leaves	Pb	ICP-MS[1]	18 – 29 ppm
(n=3)	Zn	ICP-OES	108 – 256 ppm
	Cd	ICP-MS[1]	1.9 – 3.7 ppm
	Sb	INAA	0.05 – 0.07 ppm
Acacia aneura	Ag	ICP-MS[2]	< 0.01 – 0.02 ppm
Phyllodes	Pb	XRF	35 – 64 ppm
(n=4)	Zn	XRF	190 – 445 ppm
	Cd	ICP-MS[2]	0.32 – 0.77 ppm
	Sb	ICP-MS[2]	0.2 – 0.4 ppm
Acacia victoriae	Ag	ICP-MS[2]	0.01 ppm
Phyllodes	Pb	XRF	32 – 34 ppm
(n=2)	Zn	XRF	331 – 349 ppm
	Cd	ICP-MS[2]	2.67 – 2.85 ppm
	Sb	ICP-MS[2]	0.3 – 0.4 ppm
Sida petrofila	Ag	ICP-MS[2]	< 0.01 ppm
Twigs	Pb	XRF	47 – 152 ppm
(n=2)	Zn	XRF	84 – 211 ppm
	Cd	ICP-MS[2]	0.83 – 4.34 ppm
	Sb	ICP-MS[2]	0.3 – 0.5 ppm

*Assay Laboratories: ICP-MS[1] (Becquerel Laboratories, Lucas Heights); ICP-MS[2] (Geoscience Australia); ICP-OES (Becquerel Laboratories, Lucas Heights); XRF (Geoscience Australia); and, INAA (Becquerel Laboratories, Lucas Heights).

have been recommended when sampling for Au assays (Hulme & Hill 2004).

LOCAL SAMPLING MEDIA: TENEMENT & PROSPECT SCALE BIOGEOCHEMISTRY

Many of these studies have been based on characterising and testing the biogeochemical expression of a site of known mineralisation or a substrate of 'extreme' chemical characteristics such as ultramafic bedrock. At the local-scale, plant biogeochemistry may be useful for chemical characterisation at the individual tenement- or prospect-scale by providing a chemical signature that:

1. amalgamates the chemical characteristics of an otherwise heterogeneous sampling media; and,
2. penetrates the regolith substrate and extracts a chemical signature from specific materials that may be otherwise covered (e.g., covered bedrock or aquifers).

Many of the chenopod shrubs appear to be chemical amalgamators from within the regolith substrate overlying bedrock, such as black bluebush (*Maireana pyramidata*) at the Flying Doctor Prospect (Hill *et al.* in press), and to some extent bladder saltbush (*Atriplex vesicaria*) at the White Dam prospect, although the bladder saltbush also appear to gain chemical signatures from below the base of the transported regolith interface (Brown & Hill 2004).

Two of the best examples of plants that are deriving chemical signatures derived from weathered bedrock underlying shallow transported regolith are the prickly wattles (*Acacia victoriae*) at the Flying Doctor Prospect (Hill *et al.* in press), and the mulgas (*Acacia aneura*) that colonised aeolian regolith that overlies mafic and ultramafic bedrock (Figure 2). In these cases the surface and near-surface regolith materials have either a poor or insignificant chemical signature of the underlying bedrock, however the trees appear to have penetrated this shallow (< 5 m thick) regolith and contain chemical signatures indicative of the underlying bedrock. This characteristic is extremely important for mineral exploration programs based in areas with shallow transported regolith that extends over a very large proportion of the Curnamona Province and adjacent areas. It suggests that these trees are recommended sampling media ahead of surface transported regolith materials and the more expensive shallow drilling and costean digging.

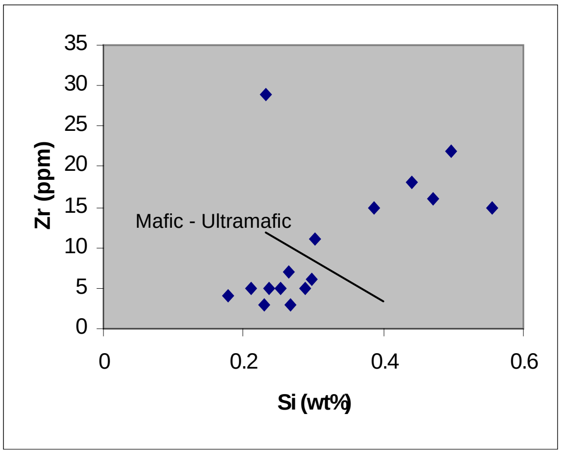

Figure 2: Mulga phyllode (*Acacia aneura*) XRF analyses for Zr and Si from trees in the Broken Hill region that are growing over mafic and ultramafic bedrock types, and a range of Willyama Supergroup lithologies. The bedrock in all of these sites is overlain by aeolian regolith up to 5 m thick.

REGIONAL SAMPLING MEDIA: WIDE-SPACED CHARACTERISATION

The two main regional biogeochemical sampling media that have been developed within this research program are river red gums (*Eucalyptus camaldulensis*) and macropod scats.

River red gums form extensive riparian woodlands along many of the major drainage lines in the region. From personal observation, their root systems seem to extend for many hundreds of metres laterally and tens of metres vertically, where they may interact with regolith substrates (mainly stream sediments), shallow aquifer systems and the underlying bedrock. Figure 3 shows some exciting assay results from a river red gum leaf sampling survey conducted along Pine Creek and extending past the Pinnacles Mine, west of Broken Hill. The very high Pb content in the leaves in the Pinnacles Mine sample, and the exponential decrease in Pb assays to eventually reach background levels (below detection limits) downstream, are typical of the results that would be expected if this chemical signature reflects a downstream dispersion plume within the stream sediment substrate. Further research by Karen Hulme involved re-sampling leaves from these trees and re-submitting ultrasonically washed and unwashed leaves for analysis. Both sets of analyses repeated the earlier assay results, indicating that the Pb is not due to Pb-rich detrital contamination on the leaves. The geochemical 'footprint' associated with other elements such as Zn covers a much greater area, thus, multi-element assays of this media may be the most useful approach in regional sampling programs.

Western NSW has been the location of some very detailed study by ecologists based at the Fowlers Gap Arid Zone Research Station, who have been trying to better understand the behaviour of kangaroos. Particular attention has been given to understanding their grazing preferences and home range (via radio tracking).

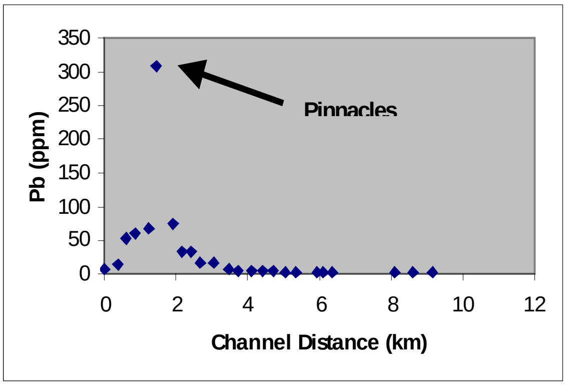

Figure 3a (left): ICP-MS analyses of Pb from trees sampled along Pine Creek passing across the Broken Hill-type mineralisation at the Pinnacles Mine. The extraordinarily high Pb content in the tree near the Pinnacles makes one wonder if a boat made of wood from this tree would float! **B (right)** Photograph of the Pine Creek catchment, looking south from the Middle Pinnacle towards The Pinnacles Mine (right). Note the riparian woodland of river red gums in the centre of the photograph.

Based on some of the results from this ecological research, sampling of scats from red and western grey kangaroos has been undertaken on an approximately 5 km sample spacing across large parts of western NSW. The assay results show high trace metal contents for elements such as Pb, Cd and Zn in the vicinity of Broken Hill and some high contents near the Pinnacles (Figure 4). These chemical signatures reside within the macerated vegetation fraction of the scats, however, it is unclear whether the high assay results centred on Broken Hill are detecting a centre of mining and previous smelting, or if they represent a natural chemical 'footprint'. Further work is being undertaken to better understand these results, however they show enormous potential for possibly being able to:

- be used as a regional chemical sampling medium across large parts of Australia to detect mineralised provinces or chemical pollution;
- reflect chemical background levels of important trace metals (e.g., at the very least the results so far show a measure for the environmental metal enrichment in the Broken Hill landscape); and,
- show that if macropod droppings are included in surface regolith samples they may account for some of the trace metal contents.

CONCLUSIONS

The results from this research have led to the development of several new and innovative biogeochemical sampling media and approaches that could be adopted in mineral exploration and environmental chemistry sampling programs, particularly based in areas with shallow transported regolith. Different biogeochemical media may be adopted for different roles including local and regional surveys, as well as for the amalgamation of otherwise heterogeneous chemical signatures with the regolith, or the penetration of transported regolith and expressing chemical signatures from the underlying bedrock.

Acknowledgements: This research program has been a component of several different research projects within CRC LEME that have received financial and in-kind support from CRC LEME, NSW DMR, PIRSA, Geoscience Australia, Pasminco Exploration (especially Tim Green), The University of Canberra, The Australian National University, The University of Melbourne, and The University of Adelaide. I would also like to thank the many different students that I have been fortunate enough to work with on many of these projects. For the results shown in Table 1, Karen Hulme and Nathan Reid are thanked for their help in sampling the river red gums at the Junction Mine, and Matilda Thomas, Karen Earl and Kylie Foster are thanked for helping to sample the other tree and shrub types from there. Thank-you also to Anthony senior and Simon Debenham for their help with sampling the river red gums from Pine Creek, and to Karen Hulme for performing ultra-sonic washing and submitting further assays from resamples of some of these trees as a part of her ongoing PhD project. The very tolerant Lea Hill helped to sample the trees and shrubs from overlying mafic and ultramafic bedrock types in the Broken Hill region. David Garnett formerly of Becquerel Laboratories, Lucas Heights is greatly appreciated for his discussions, insight and enthusiasm for accepting not only various plant samples for analysis, but also an assortment of macropod scats. David was one of the few that supported the idea of the macropod sampling and analysis when many others thought that it was crazy and would be of little interest.

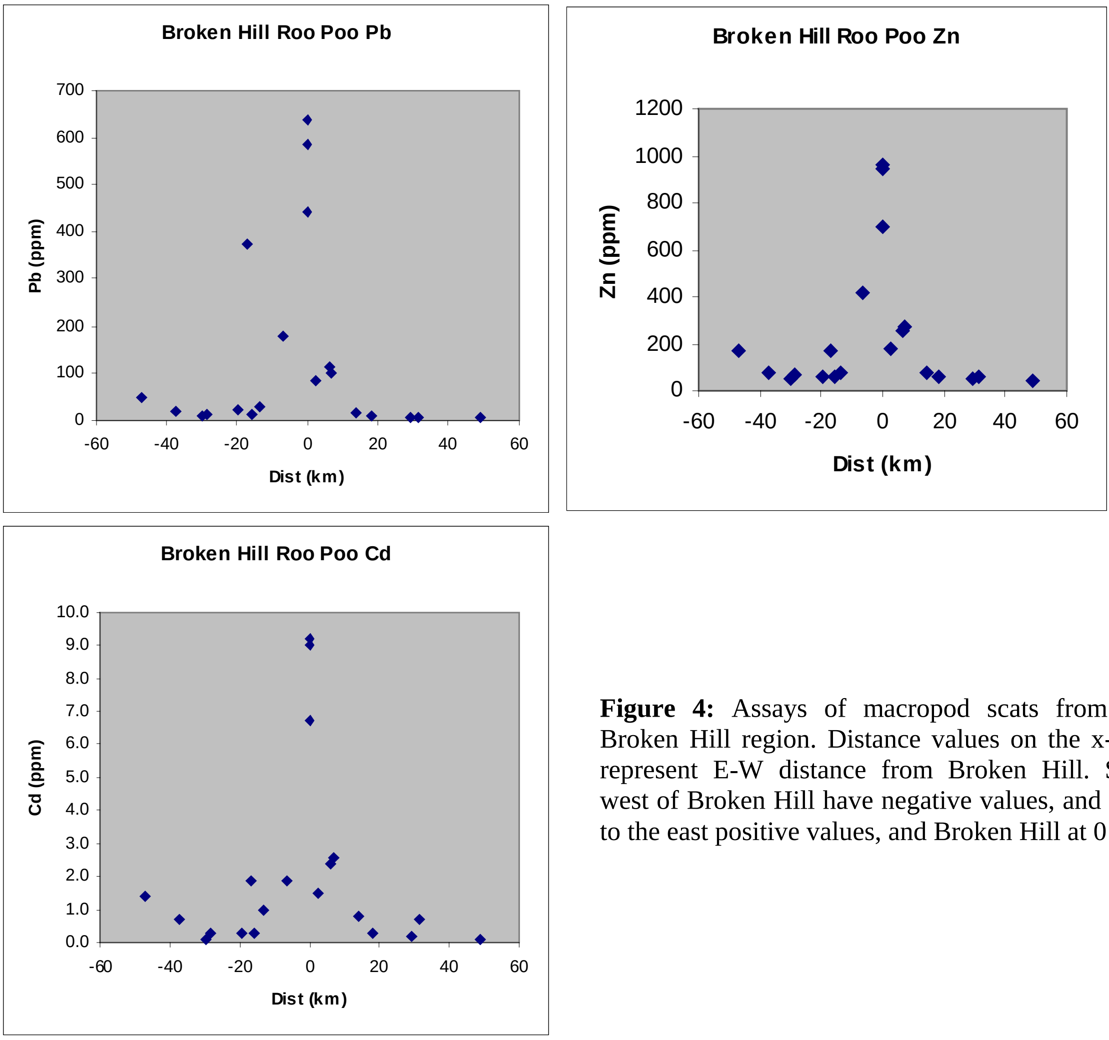

Figure 4: Assays of macropod scats from the Broken Hill region. Distance values on the x-axis represent E-W distance from Broken Hill. Sites west of Broken Hill have negative values, and sites to the east positive values, and Broken Hill at 0 km.

REFERENCES

BARRATT R.M. & HILL S.M. 2003. BHEI 2003 Mineral deposits excursion guide, Broken Hill. *Geological Survey of New South Wales* **Report GS 2003/223**.

BROWN A. & HILL S.M. 2003. White Dam – detailed regolith-landform mapping as a tool for refining the interpretation of surface geochemical results. *MESA Journal* **31**, 6-8.

BROWN A. & HILL S.M. 2004. Regolith-landform maps are an essential tool for interpreting regolith geochemistry: the White Dam, SA, experience. *In:* ROACH I.C. ed. *Regolith 2004*. CRC LEME, pp. 37-41.

DANN R. 2001. *Hydrogeochemistry and biogeochemistry in the Stephens Creek Catchment, Broken Hill, New South Wales.* B. App. Sci. Honsours thesis, CRC LEME, University of Canberra, unpublished.

DEBENHAM S.C. 2000. *Regolith-landforms and environmental geochemistry of Triple Chance east, Broken Hill, NSW.* B. App. Sci. Honours thesis, CRC LEME, University of Canberra, unpublished.

Hill L.J. 1998. *Geobotanical and BiogeochemicalAssociations at the Thackaringa Serpentinites, south-western New South Wales.* B.Sc. Honours thesis, University of Melbourne, unpublished.

HILL L.J. 2002. Branching out into biogeochemical surveys: a guide to vegetation sampling. *In:* ROACH I.C. ed. *Regolith and Landscapes in Eastern Australia.* CRC LEME, pp. 50-53.

HILL L.J. 2003. *Biogeochemical and geochemical dispersion and residence in landscapes of western New South Wales.* PhD thesis, CRC LEME, Australian National University, unpublished.

HILL S.M. 1995. Biological applications of regolith mapping. *In:* MCQUEEN K.G. & CRAIG M.A. eds. *Developments and new approaches in regolith mapping.* Centre for Australian Regolith Studies, Canberra, **Occasional Publication 3**, 69-72.

HILL S.M. 2002. Some issues and challenges for regolith-landform mapping with particular reference to the Broken Hill region. *In:* ROACH I.C. ed. *Regolith and Landscapes in Eastern Australia*. CRC LEME, pp. 63-67.

HILL S.M. & HILL L.J. 2003. Some important plant characteristics and assay overviews for biogeochemical surveys in western New South Wales. *In:* ROACH I.C. ed. *Advances in Regolith*. CRC LEME, pp. 187-192.

HILL S.M., THOMAS M., EARL K. & FOSTER K.A. in press. The Flying Doctor Ag-Pb-Zn prospect, Northern Leases, Broken Hill, NSW. *In:* BUTT C.R.M., CORNELIUS M., SCOTT K.M. & ROBERTSON I.D.M. eds. *Regolith Expression of Australian Ore Systems: A compilation of geochemical case histories and conceptual models.* CRC LEME Monograph, Perth.

HULME K. & HILL S.M. 2003. River red gums as a biogeochemical sampling medium in mineral exploration and environmental chemistry programs in the Curnamona Craton and adjacent regions of NSW and SA. *In:* ROACH I.C. ed. *Advances in Regolith.* CRC LEME, pp. 205-210.

HULME K. & HILL S.M. 2004. Seasonal element variations of *Eucalyptus camaldulensis* biogeochemistry and implications for mineral exploration: an example from Teilta, Curnamona Province, western NSW *In:* ROACH I.C. ed. *Regolith 2004*. CRC LEME, pp. 151-156.

JONES G.L. 1999. *Regolith Geology and Geochemistry of Triple Chance West, Broken Hill, New South Wales.* B. App. Sci. Honours thesis, CRC LEME, University of Canberra, unpublished.

SENIOR A.B. 2000. *Regolith Geology and Geochemical Dispersion of Pinnacles West, Broken Hill, New South Wales.* B. App. Sci. Honours thesis, CRC LEME, University of Canberra, unpublished.

SENIOR A.B. & HILL S.M. 2002. Regolith-landforms of the Pinnacles 1:25,000 sheet, western NSW: mapping and geochemical characterisation. *In:* ROACH I.C. ed. *Regolith and Landscapes in Eastern Australia.* CRC LEME, pp. 113-118.

THOMAS M., EARL K., HILL S.M. & FOSTER K.A. 2002. A framework for regolith-landform mapping in the Flying Doctor Prospect, Broken Hill, NSW. *In:* ROACH I.C. ed. *Regolith and Landscapes in Eastern Australia.* CRC LEME, pp. 127-132.