UNRAVELLING THE REGOLITH WITH GEOCHEMISTRY

Kenneth G. McQueen

CRC LEME, Department of Earth and Marine Sciences, Australian National University, ACT, 0200

INTRODUCTION
Geochemical data from the regolith can be used in five practical ways:

- To detect anomalous abundances of target and pathfinder elements during mineral exploration (or for other purposes);
- To distinguish different regolith materials (and help decipher their evolution);
- To determine the parent rock type;
- To estimate the degree of weathering and leaching of *in situ* profiles;
- To locate ferruginous zones and redox fronts, which are potential sites for accumulation/fixation of target and pathfinder trace elements.

Much has been written on anomaly detection and there has been some investigation of geochemical methods for identifying parent rocks from their weathering products (e.g. Hallberg 1984; Khider & McQueen 2005). This article focuses on the other uses of geochemical data for unravelling the regolith.

DISTINGUISHING REGOLITH MATERIALS
The regolith is composed of minerals, mineraloids, biota, water, dissolved compounds and gases. Minerals make up the largest part and determining the mineral composition is a key step in characterising different regolith materials. However, it can be difficult to identify minerals in regolith because they are mostly very fine grained or pulverised in drill cuttings (X-ray diffraction or infra red spectral analysis is generally required). Minerals have a more or less definite chemical composition and if geochemical data are available these can be used as a broad surrogate for the mineralogy.

The major primary source minerals for the regolith are feldspars, quartz, micas, mafic minerals and in some cases carbonates and volcanic glass (not strictly a mineral). These are ultimately transformed to quartz, kaolinite and iron and aluminium oxide/oxyhydroxides. The accompanying chemical changes involve addition of water, progressive loss of Na^+, K^+, Ca^{2+}, Mg^{2+} (some Si^{4+}) and retention of Si^{4+}, Al^{3+} and Fe^{3+}. The K/Al and Mg/Al ratios provide a simple index for characterising different regolith materials where they are at different stages of mineralogical/chemical evolution on the journey to end-stage regolith. Figure 1 shows the compositional distribution in terms of this index for three different types of regolith sampled down three drill holes in the Cobar region. Also shown are the typical fields for these types of regolith, based on the current data and previous work in the Kalgoorlie region (Johnson & McQueen 2001).
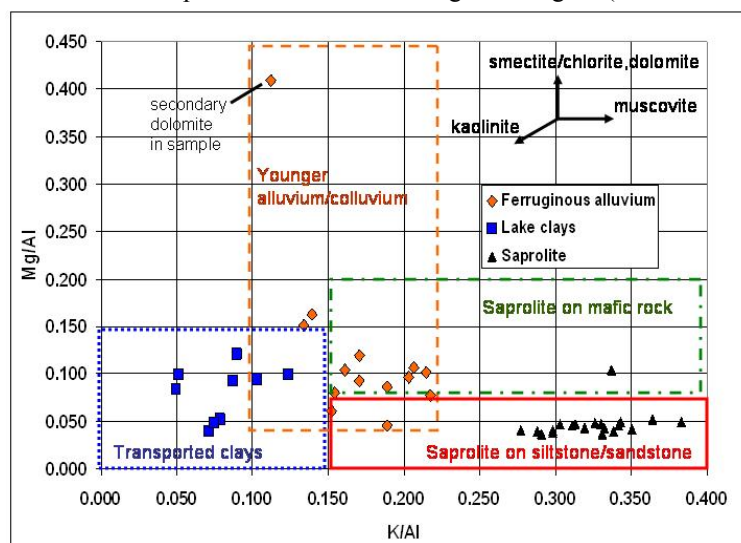

Figure 1: K/Al vs. Mg/Al ratio plot (wt. proportions) for three different types of regolith from the Cobar region of western New South Wales. Samples are 4 kg bulks from 1 m composites collected in drill holes CBAC 215, CBAC 217 and BRAC 1. Arrows indicate the major mineralogical controls on ratio trends. Also shown are the typical ratio fields for these types of regolith. Analyses by XRF.

The three different regolith materials in these examples are *in situ* saprolite/saprock, lacustrine clays (difficult to distinguish visually from weathered saprolite) and younger ferruginous alluvium/colluvium. These materials have different regolith histories that are reflected in their mineral and chemical composition. The lacustrine clays were deposited in the Late Mesozoic to Early Cenozoic and appear to have been derived

from a deeply weathered landscape (Chan et al. 2004; Chan 2005). They were well sorted during erosion and transport to produce a kaolinite-smectite-quartz dominant sediment. The saprolite/saprock contains significant muscovite and illite, which have been variably altered to kaolinite, depending on degree of *in situ* weathering and depth in the profile. The younger alluvium/colluvium was deposited in the later Cenozoic, when climatic conditions were significantly drier and chemical weathering less intense. Erosion of less altered profiles, more limited sorting and low levels of post-depositional weathering produced material that retained significant amounts of weakly altered phyllosilicates. These sediments can also contain local concentrations of dolomitic calcrete, which will be apparent in their Mg/Al ratio. There is some compositional overlap between the three materials and the clearest distinction is between saprolite and transported clays. This approach to chemically distinguishing regolith types will work within particular regions where there are regolith components characterised by different parent rock compositions, different degrees of weathering or different histories of sorting or remixing/homogenisation during transport. The differences can be established with an orientation survey.

DEGREE OF WEATHERING/LEACHING

The Chemical Index of Alteration (CIA) has been widely used to quantify degree of rock weathering (Nesbitt & Young 1982). This index, $CIA = 100 \times Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)$, reflects the breakdown of feldspars and mica to kaolinite, but it has a major drawback in that it estimates the total history of chemical weathering from the primary source rock, i.e. including that already present in sedimentary rocks prior to further weathering. It is thus difficult to apply this index as a direct measure of the *in situ* weathering of a particular regolith sample. However, it can be useful for comparing samples within profiles developed on a variably weathered common rock type (Figure 2).
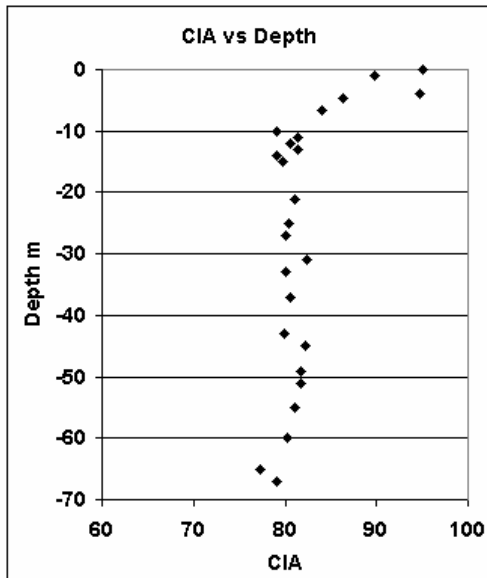

Figure 2: Plot of CIA vs. sample depth for saprolite/saprock samples from four profiles developed on siltstone/sandstone units from the Cobar region. Due to the presence of calcite (i.e. non-silicate CaO) in some of these samples, the mole proportions of CaO used in the CIA have been set equal to those of Na_2O where they otherwise exceed this value (i.e. assuming CaO in plagioclase, McLennan 1993).

Weathering trends within a profile or group of profiles on common rock types can also be distinguished using the relative mole proportions of Al_2O_3, $(CaO+Na_2O+K_2O)$ and (total Fe_2O_3+MgO). Figure 3 shows an example of an A-CNK-FM plot for samples from one of the Cobar regolith profiles. This approach is complicated by inclusion of Fe, which can be accumulated at redox boundaries or rapidly mobilised from Fe-bearing carbonates in weathering sedimentary rocks. Formation of secondary dolomite can also complicate Mg contents of strongly weathered regolith (not corrected for in the MgO mole proportion).

Figure 3: A-CNK-FM plot (Nesbitt & Young 1989) of regolith samples from profile CBAC 217. The connecting line shows the compositional path from saprock (closed lowermost square) to progressively weathered saprolite (open squares). Also shown is the trend of igneous rock compositions from the Fe_2O_3+MgO apex to feldspar and the typical weathering trend for sedimentary rocks.
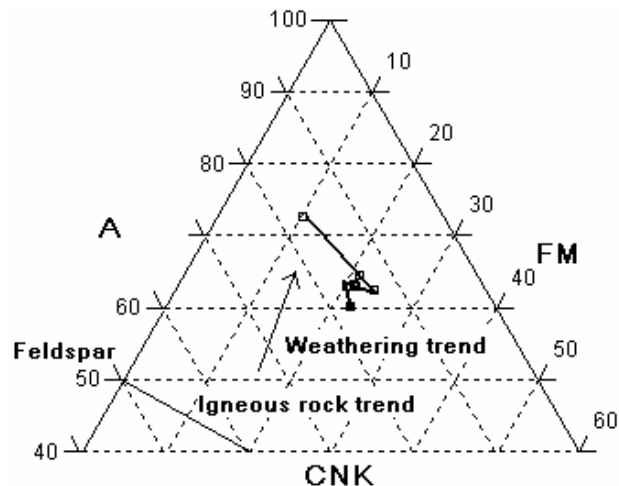
The Rare Earth Elements (REE) are commonly used as petrogenetic indicators because of their similar chemical properties, typically low solubilities and assumed resistance to fractionation in supracrustal environments. However a number of studies have shown that under some weathering conditions REE are significantly mobilised and fractionated (e.g. Nesbitt 1979; Duddy 1980; Banfield & Eggleton 1989; Sharma & Rajamani 2000). Analysis of REE distributions through deeply weathered profiles in the Cobar region indicates significant leaching in the upper parts and enrichment in the lower zone close to the weathering front (Figure 4). The LREE, particularly Ce, appear to have been the most mobile under the weathering conditions that pertained in this region. This pattern is less marked in the least weathered profiles and there is also some indication that profiles in different settings have different patterns of REE mobility and enrichment. The REE may thus provide a basis for evaluating the extent and intensity of chemical weathering and leaching. Comparison of Ce (the most mobilised LREE) with Nd (another LREE with similar properties and initial distribution) is one possibility for a REE mobility and weathering index. Examples of Ce/Nd plots for different weathered profiles in the Cobar region are shown in Figure 5. Departure of the Ce/Nd ratio from the initial ratio (typically around 1.5 to 2.5 for sedimentary rocks) indicates the relative depletion or enrichment of Ce and provides an indication of the chemical leaching of profiles.
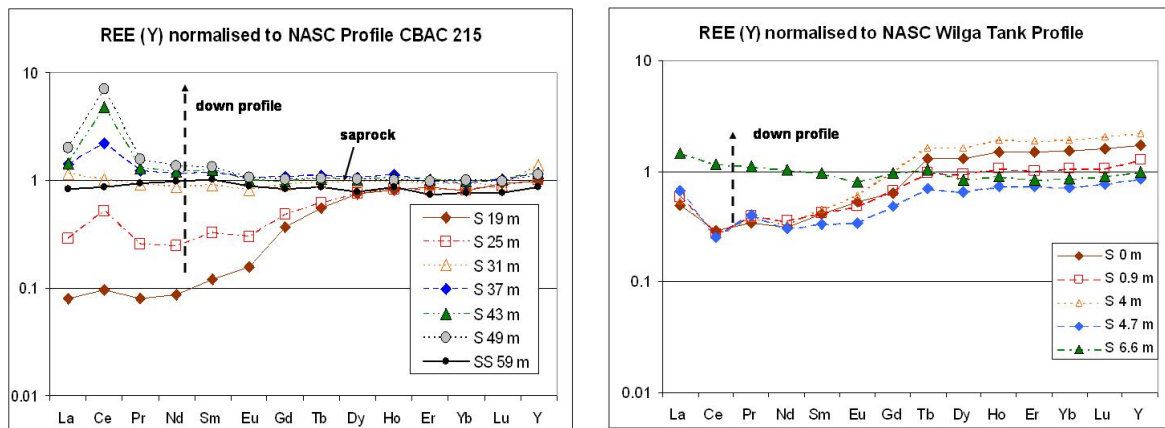
Figure 4: REE patterns for samples from different depths in weathered *in situ* saprolite from the Cobar region (examples are from the CBAC 215 and Wilga Tank profiles, REE analysis by ICP MS on dissolved fused glass discs). Data are normalised to North American Shale composite (Gromet et al. 1984).
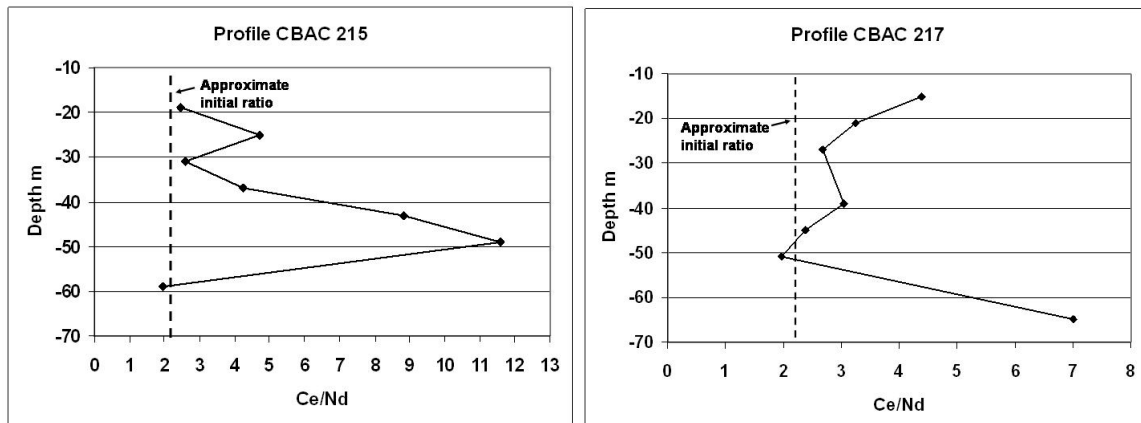

Figure 5: Variation in Ce/Nd ratios with depth in two weathered profiles from the Cobar region. The bedrock is interbedded siltstone-sandstone with Ce/Nd ratio of ca. 2.2. Departure from this ratio shows the relative depletion and enrichment (mobility) of Ce relative to Nd.

FERRUGINISATION

Ferruginisation in the regolith is controlled by reduction/oxidation of iron in solution. The resulting iron oxides/oxyhydroxides overprint other regolith materials and for this reason Fe content is not a good parameter to use in some other aspects of regolith characterisation. However, ferruginisation can indicate the position of redox boundaries, which are important chemical transition zones in the regolith. Ferruginisation also promotes trace element fixation due to the abilities of goethite and hematite to adsorb and/or incorporate

many of these elements (particularly the target and pathfinder elements used in geochemical exploration such as As, Ba, Bi, Cu, Pb, Sb, Zn). Ferruginisation and the location of potential redox boundaries can be estimated by visual observation, but this is prone to error due to the ability of small amounts of finely divided hematite to strongly colour clay-rich regolith. Short wave infra-red spectral analysis (e.g. using the ASD) can give a more reliable estimate of iron oxides/oxyhydroxides.

The Fe_2O_3 content of regolith is an obvious potential indicator of ferruginisation, however this is affected by the relative abundance of quartz and other Fe-free minerals in the sample (i.e. a very small increase in Fe_2O_3 could be very significant in a weathered quartz-rich sandstone). Comparing total Fe against an 'immobile' element can provide a more precise index, the difficulty in strongly weathered regolith is finding an 'immobile' or 'near immobile' element. Probably the best candidate is Zr, as it is largely concentrated in zircon, a resistate mineral that is remarkably stable under most weathering conditions. A problem is that zircons are not uniformly distributed in many rocks, particularly sedimentary rocks where the sediments have undergone sorting. Also Zr is a trace element, meaning small variations in its abundance can make a large change to comparative ratios. Titanium is also considered a relatively immobile element and is more abundant and widely hosted than Zr, although in sedimentary rocks a significant proportion is hosted in rutile and ilmenite, which can also be affected by sedimentary sorting. Titanium oxyhydroxide is the least soluble of the hydroxides and carbonates of the major and minor elements in near neutral dilute solutions (Garrels & Christ 1965). Variation in the Fe/Ti ratios for weathered profiles from the Cobar region highlights the zones of ferruginisation and potential redox boundaries (Figure 6).
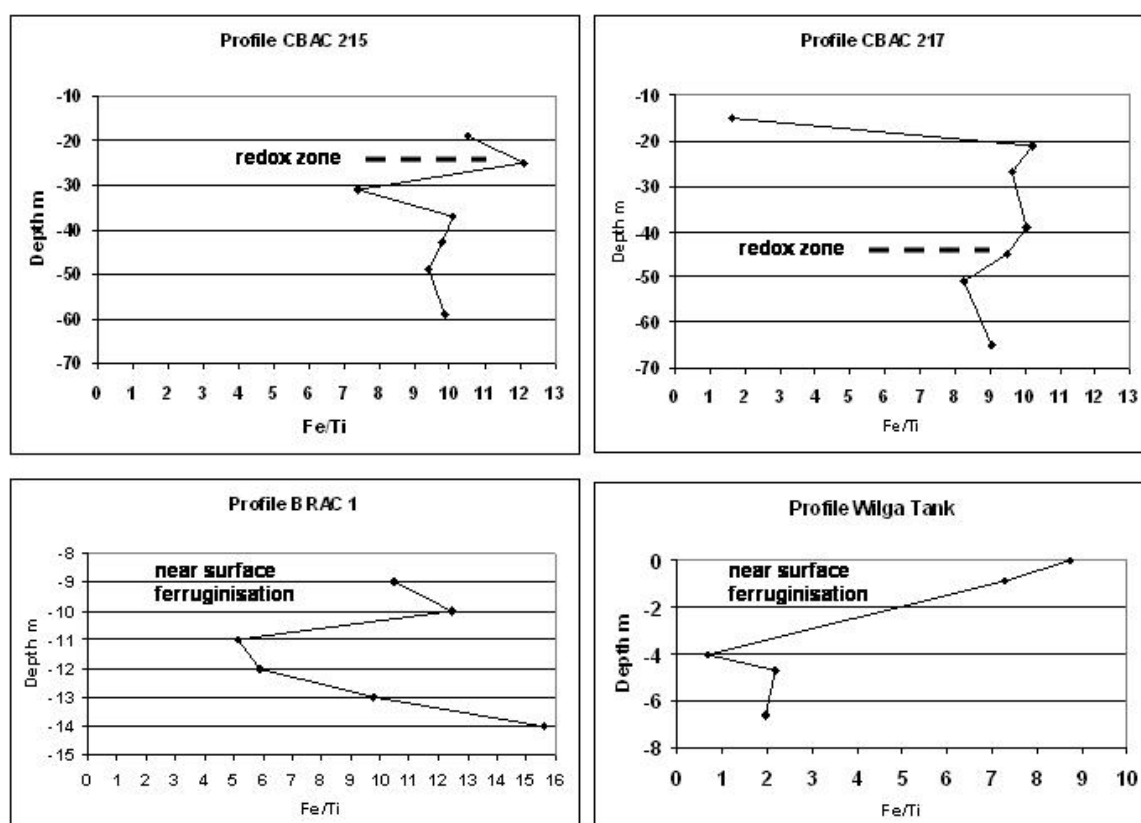
Figure 6: Variation in the Fe/Ti ratio through four saprolite profiles from the Cobar region. The top two profiles show ferruginsation at depth reflecting a redox zone. The lower examples show near surface ferruginisation

Of the major elements Al is typically the least mobile during weathering, so comparison of total Fe and Al content may also be useful in detecting the level of ferruginisation, particularly in weathered sedimentary rocks with highly variable quartz content. Aluminium is more likely to be included in the element suite for geochemical exploration programs when using multi-acid digest and ICP OES analysis. Even if Ti is included in this suite, the analyses will be less than true values due to partial or non digestion of rutile and ilmenite. Figure 7 shows a plot of Fe/Al vs. Fe/Ti for saprolite samples from the Cobar region (analysed by XRF, which gives total values for both Al and Ti). There is generally good positive correlation of these

ratios, suggesting that for these weathered profiles Al is relatively immobile. The least weathered saprock samples plot in the centre of the range of values with a trend to lower ratios with leaching of Fe from saprolite and a trend to higher ratios with ferruginisation. In a single profile, the change from a negative (leaching) trend to a positive (ferruginisation) trend will typically mark the redox boundary as reflected by iron oxide/oxyhydroxide precipitation.
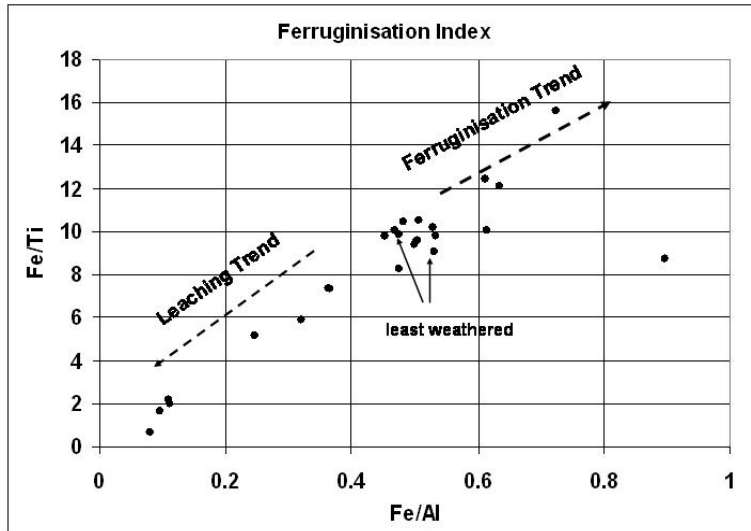
Figure 7: Plot of Fe/Al vs. Fe/Ti (wt. proportions) for saprolite samples from the four weathered profiles in the Cobar region. These show evidence of both iron leaching and ferruginisation.

DISCUSSION

Different weathering and erosional regimes can produce regolith with different mineralogical and chemical characteristics. In this way landscape evolution leaves a geochemical signature. This signature can in turn be used to differentiate regolith materials with different regolith/landscape histories. Element mobility and dispersion in the regolith varies with the extent of chemical weathering and leaching. Changes in major element and key trace element contents down regolith profiles can provide clues to the extent and history of chemical weathering and help predict zones of trace element depletion and accumulation. Ferruginsation, resulting from groundwater mobilisation of Fe^{2+} under reducing conditions, followed by oxidation to Fe^{3+} and precipitation of goethite and hematite, is a particularly important control on the accumulation of target and pathfinder elements used in geochemical exploration. Some basic interpretation of the major and trace element contents of drill cuttings can locate ferruginous zones and redox boundaries in the regolith profile. Clearly it is important to collect and analyse regolith samples through complete weathering profiles. In a major exploration program it may not be possible to sample every drill hole in this way but sufficient holes should be sampled to provide a good understanding of the three dimensional chemical structure of the regolith. This knowledge can then be used to select the most appropriate regolith horizon/s for sampling.

Modern analytical methods allow for relatively cheap and efficient collection of multi-element data. In many cases much of it is not fully utilised. It is possible to get more information from these data to improve interpretation of regolith materials and their controls on trace element distributions. The results presented here are based on high quality XRF analyses. Investigation of data acquired by the cheaper and more widely used (by the mineral exploration industry) multi acid 'total digest' method, followed by analysis using ICP OES, reveal that these data can be applied but with some caution due to the less than total analysis of K and to a lesser extent Al. Lower K results are due to the formation of insoluble potassium perchlorate during digestion. It should be possible to address this issue and improve the useability of these data.

CONCLUSIONS

Three simple chemical indices, which are easily applied, can be used to get a better understanding of the regolith. These are

- A compositional index based on the K/Al and Mg/Al ratios for differentiating regolith derived from distinctly different parent materials or with a contrasting history of formation;
- A weathering/leaching index using variation in CIA values within profiles; and
- A ferruginisation index based on Fe/Ti ratios (or alternatively Fe/Al) of regolith samples through the weathered profile.

Far from being immobile, REE can be significantly redistributed during weathering, particularly under acidic conditions, to the point where their depletions in one part of the profile and subsequent enrichments in other parts can provide an index for the intensity and style of chemical weathering.

REFERENCES

BANFIELD J.F. & EGGLETON R.A. 1989. Apatite replacement and rare earth mobilisation, fractionation and fixation during weathering. *Clays and Clay Minerals* **37**, 113-127.

CHAN R.A. 2005. Girilambone regolith and landscape evolution. *In:* ROACH I.C., ed. *Regolith 2005 – Ten Years of CRC LEME*. CRC LEME, pp. 43-48

CHAN R.A. GREENE R.S.B., HICKS M., LE GLEUHER M., MCQUEEN K.G., SCOTT K.M. & TATE S.E. 2004. Regolith architecture and geochemistry of the Byrock area, Girilambone region, north-western NSW. *CRC LEME* **Open File Report 159**, 71 pp.

DUDDY I.R. 1980. Redistribution and fractionation of rare-earth and other elements in a weathering profile. *Chemical Geology* **30**, 363-381.

GARRELS R. M. & CHRIST C. I. 1965. *Solution, Minerals and Equilibria*. Harper & Rowe, New York, pp. 403-429.

GROMET I.P., DYMEK R.F., HASKIN L.A. & KOROTEV R.L. 1984. The "North American Shale Composite": its compilation, major and trace element characteristics. *Geochimica et Cosmochimica Acta* **48,** 2469-2482.

JOHNSON C.B. & MCQUEEN K.G. 2001. The nature of gold-bearing palaeochannel sediments in the Gidji area north of Kalgoorlie, Western Australia. *Quaternary International* **82**, 51-62.

HALLBERG J.A. 1984. A geochemical aid to igneous rock identification in deeply weathered terrain. *Journal of Geochemical Exploration* **20**, 1-8.

KHIDER, K & MCQUEEN K.G. 2005. Geochemical discrimination of weathered bedrock in the Hermidale-Byrock region of western NSW. *In:* ROACH I.C., ed. *Regolith 2005 – Ten Years of CRC LEME*. CRC LEME, pp. 170-175.

MCLENNAN S.M. 1993. Weathering and global denudation. *Journal of Geology* **101**, 295-303.

NESBITT H.W. 1979. Mobility and fractionation of rare earth elements during weathering of a granodiorite. *Nature* **279**, 206-210.

NESBITT H.W. & YOUNG G.M. 1982. Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature* **299**, 715-717.

NESBITT H.W. & YOUNG G.M. 1989. Formation and diagenesis of weathering profiles. *Journal of Geology* **97**, 129-147.

SHARMA A. & RAJAMANI V. 2000. Major element, REE, and other trace element behaviour in amphibolite weathering under semiarid conditions in southern India. *The Journal of Geology* **108,** 487-496.