STATISTICAL METHODS FOR DETERMINING GEOCHEMICAL RESIDENCE IN MINERAL PHASES: EVALUATION OF PEDOGENIC CALCRETE TRACE ELEMENT DATA

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SCIENTIFIC OBJECTIVE

The development of selective or sequential extraction procedures for geochemical exploration programs requires intensive chemical experimentation with special attention to factors such as leaching time, temperature, grainsize and the type and concentration of leachate used in the extraction experiment. Considerable experimental error is also introduced during the chemical reaction through differences in the leachability of trace elements from different minerals as well as resorption onto suspended clay particles during the extraction procedure. The current study examines the use of statistics for determining the residence phases of trace elements utilising alternative methodologies using whole-rock geochemical data analysed from pedogenic calcrete and parent material sampled in profiles from South and Western Australia. The aims being to determine the geochemical changes that occur in the zone of calcium accumulation, i.e. does the minor and trace element composition of pedogenic calcrete reflect the detrital component (parent material residue or windblown aeolian input) such as quartz, clays and lithic fragments diluted only by carbonate; or are certain trace elements associated with calcium in the pedogenic calcrete profile?

CHEMICAL AND STATISTICAL METHODS AND RESULTS

Whole-rock elemental compositions of pedogenic calcrete sampled from profiles were determined by instrumental neutron activation analysis (INAA) at Becquerel Laboratories, Lucas Heights, Sydney. The suite of 30 elements analysed include rare earth elements La, Ce, Sm, Eu, Tb, Yb and Lu; transition metals Ag, Cr, Co, Au, Fe, Hf, Mo, Sc, Ta, W, Zn and Zr; metalloids Sb, As, and Te; alkali metals Na, K, Rb and Cs; alkaline earth metals Ba and Ca; the halogen Br; and the actinides U and Th. Ag, Mo, Ir, Te and Se were below detection in all samples.

The methods used to examine the data include graphing every element concentration versus depth of sample and constructing scatter-plots of the element concentrations within individual profiles to check for linearity and co-varying trends within samples from the same profile. Pearson's correlation coefficients were calculated for every combination of elements within each profile. The purpose of identifying co-varying trends between elements is to match correlated elements; two elements with positive co-variation are likely to be associated with the same residual mineral phase. Note however that these types of calculation are statistical rather than purely mathematical or chemical and the resulting clusters should be treated as probable rather than definite correlations. Elements with negative co-variation with respect to calcium suggest dilution associated with displacive calcrete growth. Further statistical analysis using ratios calculated from all the possible combinations of elements was carried out on each profile. The use of element ratios to standardise

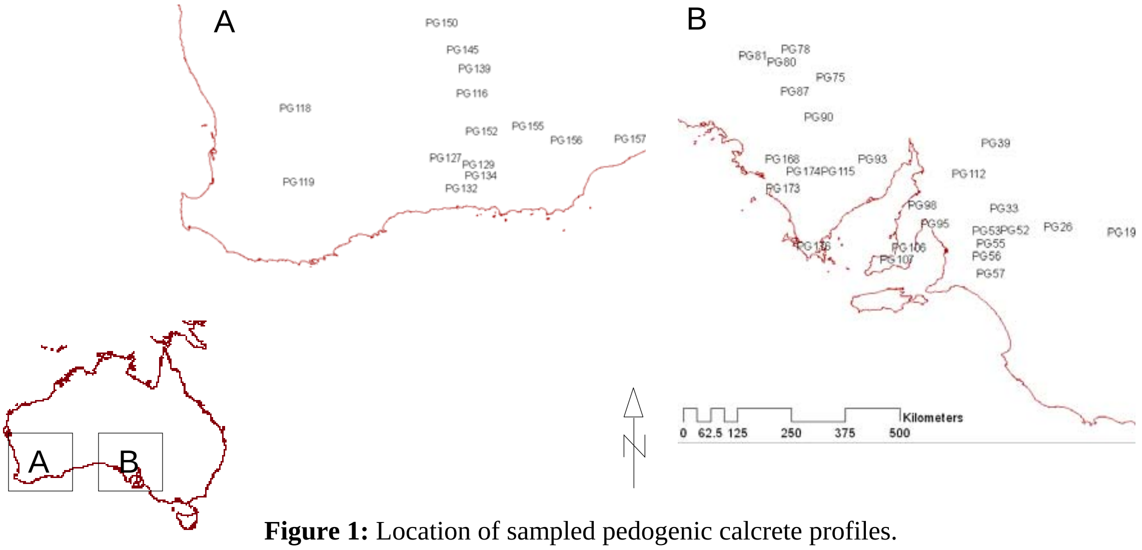

Figure 1: Location of sampled pedogenic calcrete profiles.

the data in this manner alleviates problems associated with variation in concentration of samples within profiles and parent material. A coefficient of variation is used to determine which ratios remain constant within individual profiles, a constant ratio indicating two elements associated within a particular mineral phase. This coefficient is calculated by dividing the standard deviation by the mean of the samples within each profile (including parent material), thus providing a normalised measure of variation of the element ratios through the profile. A computational method was devised in order to determine which combinations of elements group together. The logic for this method ranks the coefficient of variation for element ratios within each profile then groups them according to every element, i.e. within each profile every element is ranked according to the corresponding element in order of the coefficient of variation. If an element shows interrelation by ranking highly with a corresponding element, and the corresponding element also ranks highly with the initial element, the two are considered to correlate.

Table 1: Calcrete-gold concentrations and element clusters calculated by ranking corresponding element ratios on the basis of their coefficient of variation. * Sites have parent material sampled, n = number of samples.

Site no.	Element Associations	Calcrete-gold association	Parent Material and Location
Site 19 *n = 9	Ce-Fe-K-Rb-Sc-Th-Zn Eu-La-Sm-Yb Hf-Zr	2.6 ppb Au in calcified soil at 0.8m, else below detection	Sandy aeolian dune, northwest Victoria
Site 26 *n = 7	As-Br-Cs-K-Sb Ce-Hf-La-Th-Zr Fe-Sc Eu-Sm-Yb	3.1 ppb base of hardpan, 2.5 ppb in lacustrine, else below detection	Dolomitic Blanchetown Clay, Murray Basin SA
Site 30 *n = 6	Cr-Cs-Fe-Rb-Sc Br-Na-U Ce-Th-Yb Eu-La-Sm As-Zn	Variable within hardpan up to 3.8 ppb Au, host up to 6.8 ppb	Dolomitic Blanchetown Clay, Murray Basin SA
Site 33 *n = 4	Cs-Fe-K-Rb-Sc As-Cr-Hf-Sb-Zn Ce-Sm-Th-Yb	Max. 7.8 ppb Au in hardpan, host below detection	Dolomitic Blanchetown Clay, Murray Basin SA
Site 39 *n = 7	Cs-K-Rb-Zn As-Cr-Hf-Sb-Zr Sc-Th-Yb Ce-Eu-La-Sm-Ta	Nodules up to 5.0 ppb Au, host below detection	Dolomitic marine mudstone, Flinders Ranges SA
Site 51 *n = 7	Fe-Sc Hf-Na Rb-Zr Eu-La-Sm-Yb	Hardpan 2.5 ppb Au, host below detection	Weathered Tertiary marine limestone, Murray Basin SA
Site 52 *n = 7	Cs-Fe-Sc Ce-Cr-Th Br-Hf-Sb Ca-Zr Eu-La-Tb-Sm-Yb As-U	Hardpan up to 5.9 ppb Au, host below detection	Dolomitic Blanchetown Clay, Murray Basin SA
Site 53 *n = 4	Cs-Fe-Zn Cr-Eu-La-Sm-Tb Ta-Na Ce-Th-Yb As-Br-Ca Hf-Zr Rb-K	Hardpan up to 5.6 ppb Au, host below detection	Weathered granitic terrain, southeast SA
Site 54 *n = 6	Cr-Fe-K-Rb Sc-Cs-Zn Ta-Na Hf-Zr Ce-Eu-La-Sm-Tb-Th-Yb As-Br-Ca	Nodules up to 7.4 ppb Au, host below detection	Weathered granitic terrain, southeast SA
Site 55 *n = 7	Fe-Sc Cs-Rb Ba-Ce-Cr-Na-Sm-Ta-Tb-U-Zn-Zr	Hardpan and calcified soil up to 7.1 ppb Au, host below detection	Weathered Black Hill Norite, southeast SA
Site 56 *n = 7	Fe-K-Sc Cs-Rb-Zn Br-Ca-Na-U Ce-La-Th-Sm-Yb	Below detection	Loose yellow carbonate soil, Murray Basin SA
Site 57 *n = 8	Cs-Fe-K-Rb-Sc Ce-La Sm-Th-Yb As-Br-Na-U	Below detection	Loose yellow carbonate soil, Murray Basin SA
Site 75 *n = 6	Fe-Sc As-Cr-Cs-Yb Hf-Ta-Th Eu-Na-Rb-Sb-Sm Br-Ca	Hardpan and calcified soil up to 6.7 ppb, host below detection	Lithified red-brown sandstone, Gawler Craton central SA
Site 78 *n = 5	Ce-Cr-Fe-K-Sc-Th Ba-Sb As-Eu-Sm-U-Yb-Zn Br-Ca Hf-Zr	Calcified soil up to 7.7 ppb Au, host below detection	Lithified red-brown sandstone, Gawler Craton central SA
Site 80 *n = 4	K-Rb Cr-Yb-Zn Sc-Tb Ta-Th-Zr Ce-La-Na-Cs Sm-Eu Br-Ca Fe-U	Laminar calcrete and calcified soil to 11.4 ppb, host below detection	Weathered metagranite, Gawler Craton central SA
Site 81 *n = 7	Fe-Hf-Sc K-Rb Ce-Rb-Ta-Th Na-Sb Eu-La-Sm-Tb-Yb Br-Ca	Platy calcrete and infiltration veins to 19.7 ppb, host below detection	Siliceous metasediment, Gawler Craton central SA
Site 87 n = 4	As-Rb Ce-Fe-Sc-Th La-Yb Br-Na Sm-Eu Hf-Zr	2.6 ppb Au in surficial laminar calcrete, else below detection	Sandy aeolian dune, northern Gawler Craton central SA
Site 90 *n = 5	As-Br-Fe-Sc-Zn Rb-Th-Yb Ba-Cs-K Ce-Eu-Sm-Tb-U Hf-Zr	Below detection	Alluvial/fluvial red-brown sandy clay, Gawler Craton central SA
Site 93 n = 5	Fe-Sb-Zn As-Ce-Cr-Sc Br-Na-Rb-K Eu-La-Sm-Tb Ca-Cs-Ta-Th-U Hf-Zr	Low concentrations up to 3.1 ppb Au in hardpan and nodules	Alluvial/fluvial red-brown sandy clay, Gawler Craton central SA
Site 95 *n = 6	Cr-Fe-Sc Rb-Th-Zr Hf-Ta Ba-La-Tb-Yb Eu-Sm Br-Ca	Below detection	Sandy aeolian dune, southeast SA
Site 98 n = 4	As-Fe-Hf-Sc-Th Cr-Eu Ce-La-Sm Ba-Sb Ta-Yb Cs-Rb Na-U	Low concentrations up to 3.4 ppb Au in (basal) calcified soil	Undifferentiated calcrete plain, southeast SA
Site 101 n = 5	Ba-Ce-Cr-Th-U-Yb Fe-Sc-Th Ba-Eu-Sm Ca- Br	Below detection except 2.7 ppb Au in (upper) hardpan	Undifferentiated calcrete plain, Yorke Peninsula SA
Site 102 n = 5	Ce-Fe-Hf-La-Sc As-Ba-Ca-Sb-U-Zr Cr-Sm-Th-Yb Cs-Eu-K-Rb Br-Na	Below detection except 2.5 ppb Au in (basal) calcified soil	Undifferentiated calcrete plain, Yorke Peninsula SA
Site 106 n = 5	Cr-Cs-Fe-Sc Ba-Ca-Na-Sb-Zr As-Hf-Th Ce-Yb Eu-La-Sm	Variable within profile with concentrations up to 3.0 ppb Au	Undifferentiated calcrete plain, Yorke Peninsula SA
Site 107 n = 5	Cr-Fe-Sc Br-Na Cs-Zn Eu-Sm-Th-Yb Ce-La	Variable within profile with concentrations up to 3.4 ppb Au	Loose yellow carbonate dune (recent), Yorke Peninsula SA
Site 112 n = 4	Fe-Rb Cr-Sc-Th Sb-U-Zr Yb-Cs Eu-La-Sm-Tb Br-Ca	Low concentration with hardpan enriched up to 3.6 ppb Au	Alluvial/fluvial red-brown sandy clay, Flinders Ranges SA

Table 1: continued…

Site no.	Element Associations	Calcrete-gold association	Parent Material and Location
Site 113 *n = 6	Cr-Fe-Hf-K-Rb-Sc-Ta-Tb Eu-Yb Ce-La-Sm-Th-Zn Ba-Br-Ca	Hardpan concentrations up to 7.6 ppb Au, host below detection	Sandy aeolian dune, Gawler Craton central SA
Site 114 *n = 6	Cr-Cs-Fe-Sc La-Sm-Tb-Yb-Eu-Sm As-Sb Br-Na	Hardpan concentration up to 3.9 ppb Au, host below detection	Alluvial/fluvial red-brown sandy clay, Gawler Craton central SA
Site 115 n = 4	Cr-Sm-Yb Ce-Fe-La-Sc-Th As-Ca Br-Na Hf-Zr	Below detection	Alluvial/fluvial red-brown sandy clay, Gawler Craton central SA
Site 116 *n = 4	Ba-Br-Sb-U Rb-Ta As-Fe Th-Hf-Zr Cr-Eu-Hf-Th-Yb La-Sc Ce-Sm Ca-Na	Nodule concentration up to 19.8 ppb Au, host 7.8 ppb Au	Weathered greenstone, southern Yilgarn Craton WA
Site 118 *n = 5	As-Cr-Cs-Fe-Hf-Rb Ce-Na-Sc-Th Eu-La-Sm-Tb-Yb	Variable concentration in nodules to 7.1 ppb, host below detection	Deeply weathered feldspathic gneiss, Yilgarn Craton WA
Site 119 *n = 6	Cr-Fe-Hf-Sc-Th Ce-Eu-La-Sm-Tb	Calcified soil 4.9 ppb Au, Host below detection	Weathered ultrabasic, southern Yilgarn Craton WA
Site 127 *n = 6	Cr-Cs-Fe-Rb-Sc As-K Ce-Th Eu-La-Sm-Tb-Yb Na-Ta-U	Variable concentration in nodules to 11.7 ppb, host below detection	Green-brown mottled clay, southern Yilgarn Craton WA
Site 129 n = 6	Cr-Fe-Rb-Sc-Ta Ce-Eu-La-Sm-Th Eu-La-Sm Br-Na	Concentration in hardpan to 7.1 ppb Au	Undifferentiated calcrete plain, southern Yilgarn Craton WA
Site 132 *n = 6	As-Cs-K-Sb Br-Ca Cr-Fe-Rb-Sc-Ta Ce-Na-Th-Zr Eu-La-Sm-Tb-Yb	Concentration in incipient nodules to 6.6 ppm Au, host to 2.7 ppb Au	Green-brown mottled clay, southern Yilgarn Craton WA
Site 134 *n = 4	Cr-Cs-Fe-Rb As-Th Eu-La-Sm-Yb Ba-Br	Concentration in nodules up to 7.2 ppb Au, host below detection	Brown mottled clay, southern Yilgarn Craton WA
Site 138 *n = 6	As-Fe-Hf-Sb-Sc-Th Na-Rb-U Ba-Br-Ca-Ce-Eu-La-Sm-Yb	Hardpan up to 1120 ppb Au, ore grade host material	Fe-duricrust over auriferous orebody, Yilgarn Craton WA
Site 139 n = 6	As-Cr-Fe Ce-Hf-K-Rb-Th-Zn Hf-Th Eu-La-Sm-Tb-Yb Sb-Sc-Ta Br-Na-U	Concentration in calcifised soil up to 32.5 ppb Au	Colluvium, siltstone fragments in R-B clay, Yilgarn Craton WA
Site 145 *n = 5	As-Cr-Fe-Sc Ce-Eu-Sm Ba-La Hf-Ta-Zn Na-Rb-Tb-Th-Yb Br-Ca	Carbonate veins up to 98.2 ppb Au, ore grade host material	Saprolite over auriferous orebody, Yilgarn Craton WA
Site 148 *n = 5	Fe-Sc-Th Cr-Cs-Na As-U Ce-Hf-Sm-Tb-Yb Ca-Br	Incipient nodules and calcified soil to 29.6 ppb, host below detection	Alluvial/fluvial red-brown clay, northern Yilgarn Craton WA
Site 150 *n = 5	As-Fe-Th Cs-K-Rb-Sc-U-Zn Cr-Hf Eu-La-Sm-Tb-Yb Ba-Na Br-Ca	Hardpan up to 48.3 ppb Au, host below detection	Red-brown hardpan, northern Yilgarn Craton WA
Site 152 *n = 10	Cr-Hf-Rb-Sb-Ta-Zn Cs-Na-Rb-Sc Ce-La-Th Eu-Sm-Yb As-Br-Ca	Calcrete solutional veins up to 18.8 ppb Au, host below detection	Weathered basalt corestone, southern Yilgarn Craton WA
Site 155 *n = 4	Fe-Sc K-Rb Ba-Cs As-Br-Ca Ce-Eu-Hf-La-Sm-Ta-Tb Cr-Zn	Hardpan up to 8.9 ppb Au, host below detection	Feldspathic gneiss, southern Yilgarn Craton WA
Site 156 n = 4	Fe-Sc Ba-Cs Cr-Th Na-Rb-Ta Ce-Yb Eu-La-Sm-Tb Hf-Zr	Low concentrations up to 3.3 ppb Au in pisoliths	Undifferentiated calcrete plain, southern Yilgarn Craton WA
Site 157 *n = 6	Cr-Fe-Sc Cs-Hf-Rb-Th-Ta-Zr Ce-Eu-La-Sm-Yb Br-Ca	Low concentrations up to 4.3 ppb Au in rhizoliths	Tertiary Nullarbor Limestone, WA
Site 167 *n = 5	Ba-Cs-Eu-Fe-Hf-Sc K-Rb As-Cr Ce-La-Th Sm-Tb-Yb Ta-Na Br-Ca	Hardpan calcrete up to 2.8 ppb Au, host below detection	Weathered granite, Eyre Peninsula SA
Site 168 n = 4	As-Cr-Fe-Sc-Th Ba-K Br-Na-Ta Ce-La-Tb Eu-Sm Yb-Zr	Below detection	Undifferentiated alluvial/fluvial brown clay, Eyre Peninsula SA
Site 172 *n = 5	Fe-Sm-Th-Yb Cr-La Ba-Eu Ca-Cs-Na-Sc	Below detection	Coastal eolianite, Eyre Peninsula SA
Site 173 *n = 8	Cr-Eu-Fe-Sc K-Rb-Th As-Ca-Na Ce-La-Sm-Hf-Yb	Below detection	Coastal eolianite, Eyre Peninsula SA
Site 174 *n = 5	Fe-Yb Eu-Sc-Sm Ce-La As-Ca Br-Hf	Below detection	Coastal eolianite, Eyre Peninsula SA
Site 176 *n = 5	Fe-Hf-Th Cs-Sc-Th As-Ce-Cr-La Br-Eu-Na-Sm-U-Yb	Below detection	Feldspathic gneiss, Eyre Peninsula SA

Thus the process favours element ratios having a coefficient of variation that ranks highly for both elements. If either element is found to cluster with another element then the correlated element is added to the cluster. The element clusters calculated by ranking corresponding elements on the basis of their coefficient of variation calculated on the within-profile element ratios are given in Table 1. Elements are correlated to the sixth rank. Also detailed in the table are the parent material and the calcrete-gold association as determined by vertical distribution with the pedogenic calcrete profile. The sample locations are shown on Figure 1.

DISCUSSION

The associations of the analysed trace elements as indicated by statistical analysis of the geochemical data set indicate that many of the major and trace elements show a negative correlation with calcium indicating that they are partitioned within residual phases in the pedogenic calcrete. Several distinct element groupings occur within the elements as determined by Pearson's correlation coefficients and element ratios.

The rare earth elements La, Ce, Sm, Eu, Tb and Yb are associated strongly with one another. These elements have a strong affiliation for feldspars, which are present in most samples. The feldspar varieties identified by both thin section and XRD ranged from orthoclase and microcline to anorthite and albite, the later being the most common. Apart from being derived directly from granitic, gneissic and mafic parent materials, minor amounts occur in profiles developed on aeolian and fluvial parent materials indicating transported material as a source. Concentrations of Zr up to 1130 ppm present in samples indicate small quantities of transported zircon grains. Zircon is a possible host for Hf, Th and Yb and there is an association of these elements with Zr in some samples.

The relationships of the transition metals Cr, Fe, Hf, Sc and alkali metals K, Rb and Cs are complex and combinations of these elements are interrelated in various ways in the analysed samples. The strongest association occurs between Sc, Cr and Fe, these elements are likely to be associated with ferrous oxides (hematite) or ferrous oxyhydroxides (goethite). The elements Ce and Th are variably associated with the above-mentioned elements or with rare earth elements; some of these overlapping correlations may however be coincidental, occurring in profiles with few samples. The possibility that two or more phases host these elements is a factor that needs to be taken into consideration. Typically Ce shows a stronger relationship with the rare earth elements while Th is more commonly correlated with transition metals. Another example of different phases hosting trace elements is the association of Hf with Fe and Cr in profiles where Hf is not associated with Zr. The alkali metals K, Rb and Cs show a strong interrelation in many samples but are also variably associated with transition metals. Clay minerals are the likely host for these elements, however considering the limited number of elements analysed for in the dataset and the fact that pedogenic calcrete commonly contains mixtures of clay minerals with variable chemical composition it is difficult to say with certainty whether or not clay minerals are significant hosts for trace elements such as transition metals.

The highly mobile elements Br and Na show interesting interactions with respect to calcium and their distribution within the pedogenic calcrete profiles investigated. Bromine is the only analysed element to commonly show a positive correlation with Ca. The cause of this association is considered to be due to the process of evaporation causing salt accumulation and storage of this element concurrently with calcium within the profile. Bromine also shows a common correlation with Na in profiles were it is not correlated to Ca. Positive correlations between Na and Ca however are uncommon in the analysed samples. Sodium may be hosted as either halite (NaCl) in saline conditions or as a constituent of residual minerals such as alkali feldspar, the later however is considered to be a minor constituent in most cases and the frequent correlation of Na with Br suggests incorporation of Br into the crystal lattice of salt. Whether bromine is incorporated into calcite is uncertain but the fact that there is no three-way association between Ca, Na and Br indicates that salt is affecting the correlation by statistical analysis. Uranium does not show any common correlations in the statistical analysis; however, examination of the profile trends concentration versus depth shows that U concentration is typically increased at the base of a profile, particularly were the base of the profile is dolomitic. This evidence suggests the possible influence of capillary fringe ground waters contributing to the precipitation of carbonate at the base of pedogenic calcrete profiles. The concentrations of some trace elements show no systematic correlation within the sampled pedogenic calcrete profiles. Elements such as As, Ba, Sb and Zn show less common and variable association with each other and various other elements in the geochemical and statistical experiments conducted. The whole rock INAA indicates that the concentration of these elements is highly variable and, with the exception of As in some cases, are typically depleted with respect to calcium concentration. The incidental or residual origin of these elements may affect their potential as (exploration) pathfinder elements through their erratic occurence. The association with economically important minerals of these elements, in particular As, Zn and Sb, which are commonly associated with auriferous metal sulfide, vein and hydrothermal deposits and Zn also being associated with volcanic hosted massive sulfide (VHMS) and lead-zinc deposits, warrants further investigation into their geochemical and biogeochemical behaviour and use as pathfinder elements associated with pedogenic calcrete.

Gold was below detection for many samples and thus was excluded from the statistical analysis. Research by CSIRO and later CRC LEME during the late 1980s and 1990s has demonstrated that gold could be highly correlated with pedogenic calcrete overlying auriferous deposits in the Yilgarn Craton, Western Australia. Lintern (2002) has comprehensively described the CRC LEME and other published case studies to date and the methodology used in implementing and interpreting geochemical surveys using pedogenic calcrete as a sampling medium. The current study indicates that gold within pedogenic calcrete is concentrated up to an order of magnitude over the parent material concentration in seemingly un-mineralised sites. The cause of the pedogenic calcrete-gold association is yet uncertain but is almost certainly hydromorpic or biogeochemical rather than residual. Lintern (2002) considers a process whereby organic ligands (produced by soil flora and fauna) complex colloidal and chemical Au dispersed from host material. During rainfall events this relatively mobile/soluble Au is slowly redistributed towards the surface by the processes of meteoric infiltration and evaporation and/or evapo-transpiration. Similar meteoric processes presumably govern calcium distribution and after numerous rainfall events gold and calcium will become congruently distributed. Redistribution of gold to the surface through absorption by plants may also be a significant process and is confirmed by the presence of Au in plant tissues (Lintern 2002). Another factor that is potentially very important in controlling the distribution of gold and other trace elements within the regolith is the pH contrast that commonly exists between pedogenic calcrete and underlying regolith materials. Pedogenic calcrete is strongly alkaline; the high pH can reduce the chemical mobility and act as a geochemical barrier, thus trapping elements dissolved from underlying neutral to acid regolith and causing their precipitation in the calcrete horizon. Gold and zinc both have medium to high environmental mobility under oxidising and acid conditions but low mobility under alkaline conditions (Reimann & de Caritat 1998).

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