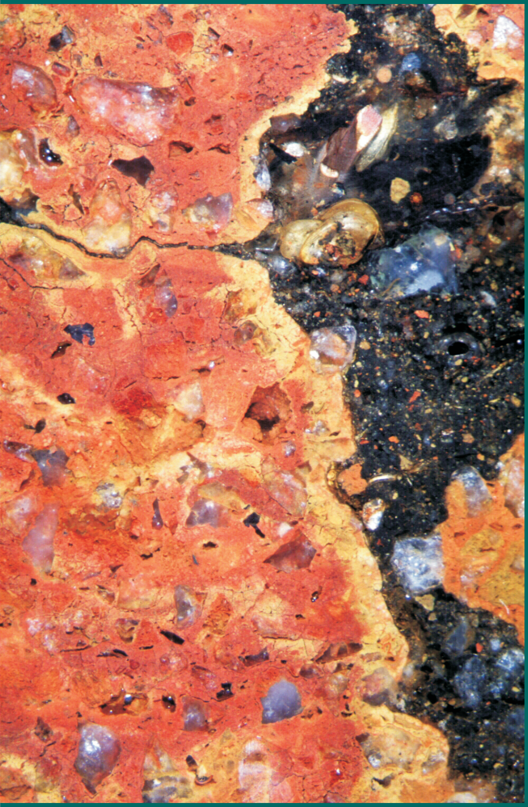
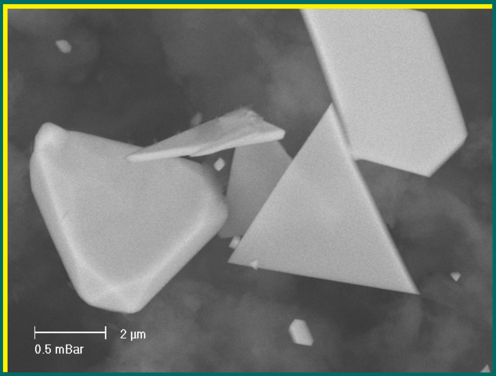
2007
MINERALS EXPLORATION SEMINAR
ABSTRACTS

28 August 2007



Ferricrete developed from grus, Pine Creek, NT

Gold nano plates



Gold in hematite

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CONTENTS

TWENTY FIVE YEARS OF REGOLITH GEOLOGY AND GEOCHEMICAL EXPLORATION IN THE YILGARN CRATON: BUTT SMITH MEDAL COMMEMORATIVE ADDRESS

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Introduction

Large areas of prospective terrain in Australia have a deep regolith, consisting of weathered rock, some cover of transported overburden. Although regolith-dominated terrains pose considerable difficulties for exploration, over the last twenty five years, regolith-dominated terrains have been receiving considerable exploration attention for finding sizeable new mineral deposits. This is largely due to a better understanding of regolith distribution, its characteristics, processes and evolution that are essential for effective design of geochemical and geophysical exploration programmes. Much of this work is summarised by Smith et al. (1992), Anand et al (1993a), Smith et al. (2000), Butt et al., (1997), Butt et al. (2000), Gray et al (2001), Anand and Paine (2002), Anand and de Broekert (2005) and Butt et al (2005).

Exploration geochemistry continues to be a major contributor to mineral exploration programmes at all scales. The last decade has spanned a complete economic cycle in the minerals industry, during which there has been a change in exploration emphasis from dominantly Au to include a range of base metals and diamonds, and the recent revival of U exploration. Increasing metal prices and the development of improved and new geochemical techniques have allowed exploration to expand to previously under-explored terrains, including those covered by thick, transported regolith. There has been significant evolution and refinement of geochemical dispersion models for transported regolith. These models have prompted further developments in sampling media, analytical techniques and approaches to anomaly detection. This paper will briefly review those advances made on the Yilgarn Craton of Australia and it will point to some important current trends in research into regolith geology and exploration geochemistry.

Regolith terminology

Regolith embraces a variety of weathered materials that are encountered in geochemical and geophysical prospecting. For researchers and exploration geologists to communicate effectively, it is important that they are able to compare and classify the regolith consistently. The first step towards mutual understanding is clarity and uniformity of terms. Over the last twenty years, various schemes and atlases have been developed for the mineral exploration industry (Anand et al., 1989; 1993b; 2002; Craig et al., 1993; Robertson and Butt, 1993; Robertson et al., 1996). Recently, a comprehensive Glossary of Regolith Terms has been compiled by CRCLEME to bring consistency and uniformity to regolith science (Eggleton, 2001).

Regolith mapping

In recent years, the importance of understanding the position of regolith materials within the regolith and the landscape for reliable geochemical exploration has become increasingly apparent. Regolith-landform mapping has gained greater importance, wider acceptance and usage within the mineral industry over the last decade. Guidelines for regolith-landform mapping are documented by Pain et al. (2001) and Anand and Paine (2002).

Regolith-landform maps are not intended as end-products but provide two key pieces of information for mineral explorers – whether near-surface material is residual or transported, and the expected thickness of transported material. Both *factual* and *interpretative (derivative)* regolith-landform maps have been produced for a number of terrains. Derivative maps are assisting in identifying probable dispersion models and subsequent design of geochemical surveys, including media selection, sampling procedures and intervals. Appropriate thresholds can then be set, anticipating and allowing for variations in geochemical responses due to weathering or masking by transported overburden. The likely effects of chemical and mechanical dispersion, resulting in displaced anomalies, can be incorporated into data interpretation.

The third dimension

Three dimensional regolith models are being built around large drill-hole datasets. For example, the Yandal project, in the Yilgarn Craton, included a 3-D representation of residual and transported regolith over a major gold system in an Archaean greenstone belt using a database of over 70,000 drill holes and high-resolution aeromagnetics (Anand, 2000; Gray et al., 2001;) and spectacularly identified the maghemite-defined palaeodrainages. These 3-D models can define the base of the transported regolith, weathering fronts, internal regolith structure and have genuine predictive value. Although difficult to construct, due to inconsistencies in regolith logging and problems defining regolith unit interfaces, there have been advances in geophysical methods for regolith mapping methods that require minimal drill-hole calibration, including the low-frequency, broad-bandwidth, time-domain TEMPEST airborne EM system (Lane *et al*., 2000). With the advent of higher resolution aeromagnetic data, and the capacity to differentiate regolith features (e.g. Fe accumulation in palaeochannels) from bedrock magnetic feature, the interaction of drainage and geology becomes clearer. A significant observation from these transported regolith models is that, despite the subdued landscapes across much of Australia, the palaeotopography below the interface is quite rugged. It is this elusive form surface that will continue to host the reliable direct geochemical indicators of buried mineral systems.

Landscape processes and models

Understanding the distribution and origin of regolith materials and palaeotopography has refined and developed new landscape evolution models (Anand and de Broekert, 2005). These models have affected the interpretation of geochemical dispersion data and anomalies. Weathering profiles have formed in both residual materials and in transported overburden of various ages. There have been several distinct periods of ferruginisation, deferruginisation, kaolinisation, silicification and calcification. Biological processes have formed mottles and pisoliths. The complex and long evolution of regolith is well known but various geochronological techniques now permit quantification. The basic geochronological framework of the Australian regolith can be provided by palaeomagnetic dating using secondary hematite formed in saprolite by chemical weathering. Palaeomagnetic dates for regolith from 30 sites throughout Australia indicate two principal weathering events at around 10 Ma and 50-60 Ma, with some evidence of Mesozoic or even earlier weathering in the eastern Yilgarn (Pillans, 2005). It is likely that each weathering event generates metal dispersion, hence dating such events may contribute to selection of more favourable geochemical sampling media - either bulk samples or minerals.

It is also now clear that ferruginous pisoliths and duricrust have formed in a variety of materials including residuum, colluvium and alluvium. In places, ferruginous duricrusts occupy elevated areas because of relief inversion. Thus, a distinction between residual and transported materials is essential for useful geochemical sampling. Morphology and dimensions of the iron mineralised structures of both cutans and cores in the pisoliths show biological processes have played an important role in their formation.

Pedogenic and groundwater calcretes are end members of a continuum that varies according to landscape setting and origin. Pedogenic calcretes occur in soils in association with a variety of rock types. Their thickness and forms are largely controlled by topographic setting and the nature of host material. Airborne accession is an important source of calcium for the formation of pedogenic calcretes, but weathering of bedrock, lateral transport by soil creep and soil solutions, and redistribution by biological processes are also important.

The red-brown hardpans are formed by partial replacement and cementation of the matrix and clasts by amorphous Si and aluminosilicates with minor goethite and hematite, accompanied by clay illuviation. Silicification of hardpan is associated with weathering within and outside soil profiles and appears to be still active.

Objective mineralogical and geochemical logging of regolith

Mineral analysis by portable spectral analytical devices, which provide rapid and detailed mineralogical characterisation, may provide indicators of mineralization and/or alteration, differentiate between residual and transported regolith and linking geochemistry with regolith, and provide a more solid interpretation of geochemical data (Phang et al., 2007)). Field-based analytical devices such as field-portable XRF have potential contributions, although understanding the *limitations* is essential.

Exploration through transported cover

Partial extraction analysis

Experimentation with partial extraction techniques, first started in the 1970s, was designed to pursue subtle, less-obvious geochemical signatures potentially swamped by background “noise”. More recent application followed the development of enhanced analytical detection limits. The basic assumption behind these techniques is that ore bodies continuously but slowly release metal ions during weathering. These ions are presumed to rise more-or-less vertically to the surface where they are variously hosted by clays, carbonates, organic matter, amorphous or crystalline Fe and Mn oxides.

Partial extractions have met with only limited success in deeply weathered arid terrains compared to recently glaciated areas. Most studies are empirical investigations of the partial extraction response of regolith components to deeply buried underlying mineralization and there has been little quantitative study of the actual mechanisms of the extractions or the mineralogical-digestion response. Partial extraction techniques clearly give positive responses and improved signal to background in shallow regolith, and there are claims of responses from ore bodies as deep as many tens of metres. However, comparative studies in different regolith environments, including transported regolith, show that weak, moderate and total dissolution methods all give similar responses in areas where the transported cover is less than 10 m and none where it is >10m (Gray et al., 1999). In general, partial extraction analyses may yield sharper anomalies, with higher contrast. What is not universally agreed upon in exploration is whether anomalies produced by labile metals work where conventional total dissolution fails. This is one of the unresolved areas of gold exploration in Australia, which is not without protagonists and sceptics on either side. Perhaps the greatest uncertainty with the partial leach techniques is the presumption of ion mobility in nature, for which the mechanisms are unknown.

Sampling media

Numerous case studies have documented the development of secondary geochemical dispersion haloes and mineralogical changes within and below the transported regolith above deeply weathered deposits in various regolith settings (Butt et al., 2005). Experience in the Yilgarn, North Queensland and Gawler goldfields suggests that sampling of soils and calcrete in areas of transported overburden of more than five metres has little predictive value in gold exploration (Butt et al, 2000; Anand, 2000; Butt et al., 2005;). Thus, sampling cannot distinguish the negative result (nothing there) from the null case (not adequately tested). Yet there are many examples of strong near-surface Au anomalies in 5 – 25 metres of transported material above known mineralisation. Some of these are mechanical redistribution of gold from residual environments. For example, false or coincidental anomalies can occur in calcrete over mineralisation, where they are derived from detrital, Au-bearing ferruginous granules sourced from distal outcropping mineralisation (Lintern, 2002). Thus, an appreciation of regolith-landform settings, in which a variety of calcrete types have developed, is essential if these materials are to be used wisely in exploration.

In depositional environments, the pre-existing weathering may either be preserved or truncated prior to deposition of the sediments, so it is essential to capitalise on any dispersion that may have been retained or developed during or since burial, such as;

(a) Dispersion in literati residuum and ferruginous sepiolite at the top of the weathered basement. These could be mechanically dispersed in the base of the colluviums-alluvium.
(b) dispersion in palaeosols developed on the partly truncated profile, now incorporated in the base of colluvium-alluvium.
(c) chemical dispersion during or after deposition of the sediments, in the palaeochannel sequences and Quaternary colluvium-alluvium, or along the unconformity. Chemical dispersion could still be active.

Even where buried, lateritic residuum is an effective sampling medium, but it is essential to distinguish it from distally transported lateritic debris (Smith et al., 2000; Anand, 2000). This significant transport is common in the sedimentary cover and may directly overlie either lateritic residuum or saprolite. Such debris is generally unrelated to the underlying material and is inappropriate as a sample medium on a local scale. Sampling of lateritic residuum should always be in a regolith-landform context to avoid inadvertent sampling of ferruginised sediments or other 'non-lateritic' material'. Iron-cemented sediments are generally unsuitable as sample media on a local scale but may contain indications of distal mineralisation, either within their detrital component or in the hydromorphically-derived goethite cement. The elements are concentrated following lateral transport from sources that may be hundreds of metres or several kilometres away. Criteria have, therefore, been established to distinguish lateritic residuum from Fe-cemented sediments (Anand et al., 2002).

Where lateritic residuum is absent, interface sampling is an important sampling medium in areas of transported cover (Robertson et al, 1996). The saprolite-transported overburden interface may incorporate residual or partly transported palaeosols and lag, with greater scope for mechanical and hydromorphic dispersion, during and after sedimentation. The material on the interface can include diverse materials from a variety of sources, depending on the degree of palaeo-exhumation of the palaeo-weathering profile, but it requires very accurate logging and targeting.

Non-regolith sampling media

In areas of transported regolith, a number of alternate sampling media to regolith are being evaluated. These include groundwater (Giblin and Mazzuchelli, 1997; Gray, 2001), soil gas (Polito et al., 2002) and vegetation (Lintern et al., 1997; Hulme and Hill, 2005; Anand et al., 2007; Reid et al, 2007). Groundwater should be an ideal sampling medium because of its interaction with the materials through which it moves. However, it has not yet proven reliable for gold search in the Yilgarn Craton particularly in the Kalgoorlie region (Gray, 2006). However, indications to date are that hydrogeochemistry is useful for base metal and possibly Ni exploration.

The greatest potential for vegetation lies in areas of transported overburden, where tap roots or even lateral roots, may reach weathered bedrock and its associated groundwaters. Initial work on selected base metal and Au deposits shows geochemical signatures of bedrock mineralisation in plants such as Eucalyptus, Acacia and Spinifex in erosional terrain and in some areas of substantial thickness (10-15 m) of transported overburden (Hulme and Hill, 2005; Anand et al., 2007; Reid et al., 2007). At most sites of thick transported overburden, total and selective extractions of target and pathfinder elements in soil from 10-20 cm depth show either no or an ambiguous response. However, there are significant differences between different organs of the plants; not all organs are equally useful. Substantial variation within the different organs of a single plant emphasises the importance of consistency in collecting a similar amount of the same organ at each location. Recently, it has been shown that microbiota resident in Australian regolith are capable of actively mediating a biogeochemical cycle of Au in the environment. Furthermore, there is evidence for a number of processes and organisms that may be associated with this cycle (Reith and McPhail, 2006).

Micro-mineral mapping

Micro-mineral mapping using *in situ* geochemical analyses at the micron scale points to new techniques of anomaly detection. One significant finding is that trace metals of Cu, Zn and Au are preferentially hosted in some specific clay minerals and alunite (Le Gleuher, 2003; Hough et al., 2005). If these hosts could be effectively beneficiated or selectively analysed they might provide a new technique to enhance the otherwise swamped anomalies.

Improved analysis

The wave of developments in selective geochemical extractions, and the implementation of large-scale geochemical surveys using these methods, has largely ridden on the back of developments in analytical methods, including progressively improved, routine, analytical sensitivities, achievable detection limits, reduction in costs and improvements in reliability of analytical devices such as ICP-MS. Some new exploration techniques, such as the use of ultra-trace stable isotopes, have also been made possible by the availability of high resolution analytical devices such as multi-collector HR-ICP-MS. For many elements, routine detection limits for geochemical samples have improved by half to one order of magnitude, with more elements being added to routine commercial multielement packages.

Future research

The detection of mineralisation in areas dominated by transported regolith remains the main challenge for exploration geochemistry, with U now added to the list of commodities. There have been some important developments over the years in regolith geology and exploration geochemistry which have become routine tools. Many of the advances over the last few years are largely incremental. They relate to enhancing known techniques and understanding regolith structure. The initial promise of selective geochemical extractions as the “quick fix” for areas with thick transported or deeply weathered cover has not materialised, but it has prompted research into the fundamental processes of geochemical dispersion in those terrains and new approaches to the definition and the detection of geochemical patterns related to underlying mineralisation. The focus for future research is to understand mechanisms that disperse indicator elements through transported cover in well controlled 3/4D regolith-landform frameworks. This will allow us to be more predictive and less empirical. The major challenge is to identify plausible mechanisms that will raise diagnostic labile elements through the vadose zone. Although there has been some important progress in understanding the physical-chemical processes in some environments, soil gas and biological processes that may in fact be dominant contributing process.

Continuing interaction between exploration geochemistry and environmental geochemical practitioners is certain – both groups ask the same fundamental questions about controls of metals in the surficial environment. There will be an increased role for isotopic analysis in terrane selection and mineralisation detection. An increasing challenge to the technical capacity of the minerals exploration sector to discover new deposits is the progressive decline in the number of universities offering geoscience programs.

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NEW PRE-COMPETITIVE DATA: THE YILGARN LATERITE ATLAS

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The Atlas provides geochemical coverage at a sample spacing (9 km) sufficiently close to recognize regional geochemical trends, major lithologies and dispersion halos around significant bedrock mineralization. The extent of the coverage (approximately 400 000 km^2) means the data are valuable for both exploration and environmental purposes. The sample medium is ferruginous nodules and pisoliths from lateritic residuum, its derived lag and ferruginous gravel selected from locally derived colluvium. All 3142 'laterite' samples were analysed for a minimum of 53 elements by XRF, ICP-OES and ICP-MS, with selected samples analysed for PGE. Considerable care was taken in monitoring analytical quality throughout.

Significant results include increased Au abundances in the northeast of the survey area that not only cluster around known gold deposits, but extend beyond them, indicating the likelihood of more widespread mineralization in these areas. A chalcophile element index illustrates potential for Au and base metal mineralization in the westernmost part of the Yilgarn Craton, whereas a pegmatophile index shows a regional northwest trend parallel to regional structures. Chromium abundances in granitic terrain might indicate mafic-ultramafic remnants (some with anomalous Au) beyond known greenstone belts. A regional Hg anomaly trends northwest for more than 500 km. Anomalous As, Bi, Mo and Sb along the south margin of the craton may be related to Au mineralization. Because the dataset is very consistent, multivariate statistics can be used to highlight specific lithologies and locate target types.

The data and an accompanying WA Geological Survey Record (2007/9) were released via the WA Geological Survey website in June 2007. The work was funded by CSIRO, CRC LEME, the WA Geological Survey and MERIWA.

NICKEL LATERITES: CHARACTERISTICS, CLASSIFICATION AND PROCESSING OPTIONS

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Nickel laterites are regolith materials that contain economically exploitable reserves of nickel (and, commonly, cobalt), in thick residual weathering profiles (regolith) on ultramafic rocks. The deposits are developed on olivine-bearing ultramafic rocks, of both ophiolitic and komatiitic affinities, and their serpentinized equivalents. The nickel is derived principally from forsteritic olivine ($>Fo_{75}$), which commonly contains 0.16-0.40% Ni.

The nickel concentrations generally occur in one or more horizons or units within the profile and the ores can be classified according to their mineralogy:

Oxide: dominated by iron oxyhydroxides, principally goethite, forming the mid to upper saprolite and extending to the pedolith. Nickel is hosted mainly in goethite, by substitution for iron and/or by adsorption. Manganese oxides (*e.g.*, asbolan, lithiophorite) are commonly abundant and are enriched in both cobalt and nickel. Deposits developed over dunites may contain abundant secondary silica. Mean grades are about 1.0-1.6% Ni.

Hydrous Mg silicate: dominated by hydrous Mg-Ni silicates in the lower saprolite. The silicates are mainly nickeloan varieties of serpentine, talc, chlorite and sepiolite, many of which are poorly defined and are known informally as “garnierite”. Globally, these ores have the highest grades (mean 1.8-2.5% Ni), and are typically found in areas of high relief, generally on ophiolitic rocks.

Clay silicate: dominated by nickel-rich smectites such as nontronite and saponite, commonly in the mid to upper saprolite and pedolith. Nickel in these minerals is fixed between structural layers or substitutes for ferric iron in the octahedral layer, with concentrations up to 4%. Mean grades are generally 1.0-1.5% Ni. The deposits form from peridotite and are typically found in areas of low relief.

Nickel laterites are found in a wide variety of present day climatic conditions, ranging from tropical to cool temperate, rainforest to semi-arid. However, all originally formed under humid savanna and rainforest conditions. Thus, whilst some deposits are still forming, some may date from as early as the late Palaeozoic, and others from the Cretaceous to the Miocene, with modification continuing to the present under changed conditions.

There are currently three main processing routes used to extract nickel from laterites, the choice dependent on mineralogy and, in part, on energy options:

- Pyrometallurgical smelting to produce ferro-nickel or nickel sulphide matte: hydrous silicate deposits. Recovery: 90-95% Ni, ~ 50% Co. Also suitable for clay silicates. Energy intensive.
- Caron process (reduction roast – ammoniacal leach): oxide deposits, with some tolerance for hydrous silicates. Recovery: ~80% Ni, 40-50% Co. Energy intensive.
- High pressure acid leaching (HPAL) with sulphuric acid: oxide and clay silicate deposits (<4% Mg) Recovery: over 90% Ni and Co as electro-nickel and nickel briquettes; or as intermediate products (*e.g.*, nickel carbonate).

In addition, various ‘atmospheric’ leaching (atmospheric pressure, ~100ºC) and heap leaching options are being trialled as lower capital cost/lower recovery alternatives for all types. Bioleaching is also being investigated as a route for treating oxides and clay silicates.

PROCESS	ORE	PRODUCT	COMMENT
Smelting 1859, New Caledonia	Hydrous silicate	Ferro-nickel matte	Energy intensive; (smelting ~1600ºC)
Caron process Reductive roast & ammoniacal leach 1944, Cuba	Oxide; hydrous silicate (Mg <4%)	Ni oxide; Ni briquettes	Energy intensive (reduction ~700ºC) low Co recovery
High pressure acid leach (HPAL) 1959, Moa Bay, Cuba	Oxide; smectite (Mg <4%)	Ni briquettes; electronickel; sulphide, oxide, carbonate	Less energy intensive. Plant & process problems
Enhanced high pressure acid leach (EPAL)	Low grade hydrous silicate	Ni-Co hydroxide	Atmospheric leach after HPAL
Atmospheric leach H_2SO_4; $HCl/MgCl_2$ (Sechol)	Oxide, smectite and/or hydrous silicate	Ni-Co hydroxide	Lower cost; lower recovery
Acid heap leach	Oxide Possibly smectite and/or hydrous silicate	Ni-Co hydroxide	Lower cost; lower recovery

NEW APPROACHES TO SOIL GEOCHEMICAL EXTRACTIONS

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Partial geochemical extraction has been used as geochemical exploration tools to detect surface soil anomalies associated with buried mineralization. Because refractory concentrations of many pathfinder elements such as Cu and Zn are typically not digested by these partial extractions, high geochemical contrasts are commonly observed in orientation surveys. The results of these surveys are thus more compelling, interpretable and visually appealing. The philosophy behind partial extractions is that they selectively strip elements from specific mineral hosts.

In an effort to gain more insight, a number of partial and complete geochemical extractions were tested and compared. These extractions included four acid, aqua regia, LocatOre®, cold hydroxylamine hydrochloride, Mehlich I reagent (weak HCl and H_2SO_4), deionized water, and four new partial extractions. The tests involved analysis of thirty <63 µm soil samples from the Wartook region of Victoria, Australia. The soils were known to exhibit Cu and Zn anomalies.

Results from the four new extractions were compared with the six traditional or previously applied methods. Minimum probability statistics were used to quantitatively measure and compare the resulting performance levels of each extraction. The four, new extraction solutions are proprietary, as the proportions of their ingredients are not publicly available, but they are readily available world-wide at low cost. Three of the four extractions do not exhibit significant regional or batch variation; the forth extraction likely exhibits minor regional and batch variation, although this probably does not influence the results. Complete disclosure of the new geochemical technique methodology will be provided in the presentation as a legacy for future scientific comparisons. Furthermore, a rigorous quality control assessment has been undertaken for each method to document the level of exploration precision and accuracy.

Results from the study indicate that the four new extractions perform well in terms of both exploration accuracy and geochemical contrast; minimum probability statistical methods confirm these conclusions. The ten extractions all exhibit elevated Cu and Zn concentrations in the anomalous zone, although some methods performed better than others. The pH in all of the new partial extractions rapidly (< 30 min) equilibrated with the soils, and remained stable for more than 8 hours (the extraction time was 2 hours). The high pH stabilities observed in the four new extractions is most likely due to the presence of many buffering, organic polyprotic, mostly carboxylic, compounds. Although most extractions successfully identified the anomalous sites, the four new extractions, plus a weak acid extraction and the hydroxylamine hydrochloride leach, performed the best. The new extractions worked particularly well in terms of accuracy and precision for Cu, whereas the hydroxylamine performed best for Zn.

Generally, results indicate that for anomalous soils, a large number of partial extraction methods will be more or less effective, but some offer an advantage over others in terms of improved geochemical contrast and exploration accuracy.

THE APPLICATION OF ISOTOPES TO REGOLITH GEOCHEMISTRY

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Isotope Systems
There are 92 naturally occurring elements in the periodic table and about another 20 ‘transuranic’ elements which have been synthesised in nuclear interaction experiments. However, there are over 2500 isotopes (nuclides) of these elements that have been discovered, and the number is constantly growing. Most of these have little value for our endeavours in measuring and understanding the processes that have helped form the Earth’s regolith and I shall concentrate in this contribution on a very small subset.

For the purposes of this talk I will categorise isotopes according to the following scheme:

- Unstable isotopes (only about 10% of known nuclides are stable)
- Stable Light isotopes
- Stable Heavy isotopes

The determination of isotope ratios can aid in:

- Estimation of the age of regolith minerals and groundwater
- The nature of the process that formed the regolith and the sources and mixing proportions of elements in the regolith.

I will deal only briefly with the first of these and concentrate on the latter.

Age Determinations of Regolith Components
The decay of *unstable isotopes*, where the rate of decay is know to a high level of accuracy, can be used to measure the age of a variety of regolith components. The main isotope system applied to mineral phases is $^{40}Ar/^{39}Ar$ which is used for K bearing authigenic minerals such as alunite. The age of groundwater can be determined by a variety cosmogenic isotope techniques including tritium (^3H), ^{14}C and ^{36}Cl. A major spike in the atmospheric production of these isotopes due to nuclear testing in the 1960’s has allowed very accurate age determinations of water and of plant material younger than that event.

Regolith Processes
The isotopic compositions of the *light stable isotopes* of C, O, H, and S vary in nature as a result of process and source. For example the $\delta^{18}O$ value of oxygen involved in both organic and inorganic reactions is temperature dependent and can indicate palaeolatitude or whether a particular regolith phylosilicate formed due to low temperature (weathering) processes or to high temperature (magmatic) processes. Distinct reservoirs of elements can also have measurably different isotopic compositions. For example, whereas the $\delta^{34}S$ value of aerosols which make their way into groundwater is dominated by seawater sulphate, S is also available to groundwater through equilibration with aquifer minerals. The difference between the atmospheric and geological source can be significant, thus allowing estimates to be made of the relative input from these two sources. As an example groundwater sulphate derived from rainwater in the Gawler Region of South Australia has a $\delta^{34}S$ value of 16 – 18‰ and sulphate derived from oxidising sulphide minerals has $\delta^{34}S$ values between -2.5 and 5.6. This allows mapping of a dispersion halo around the sulphide systems that trends for over a kilometre.

As a result of the modern generation of Inductively Coupled Plasma sourced multi-collector mass spectrometers, it is now practical to measure the isotopic composition of the elements Fe, Zn and Cu. These are very important elements because they represent major, target components of ore systems and move readily within the regolith.

Of the *heavy, stable isotopes* we shall confine ourselves here to the Sr and Pb systems. The isotopic composition of Sr (^{87}Sr/^{86}Sr) at the time of the formation of the Earth as measured from meteorites and lunar samples is considered to be 0.69897 +/- 0.00003. Over Earth history, ^{87}Rb has been decaying to ^{87}Sr and so the average ^{87}Sr/^{86}Sr of the Earth has been constantly increasing. Modern ratios depend on the ^{87}Rb /^{87}Sr integrated over geological time of the rock units being measured, and generally vary between about 0.702 and 0.720. The modern ocean has a homogeneous ^{87}Sr/^{86}Sr ratio of 0.709 and is a major reservoir for Sr involved in regolith processes. As an example, a Sr isotope study of southern Australian calcretes by LEME staff at the University of Adelaide was able to show that the Ca in the calcrete was almost exclusively derived from a marine source rather than underlying bedrock.

The Pb isotope system is perhaps the most useful as a tracer of regolith processes. Pb is a significant component of many ore systems, its variation through geological time and in different reservoirs is large and well documented and it is found in most regolith materials. The stable isotopes of Pb (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) consist of a primordial component to which has been added radiogenic ^{206}Pb, ^{207}Pb and ^{208}Pb from the decay of the unstable isotopes ^{238}U, ^{235}U and ^{232}Th respectively. Measured isotopic compositions depend on the age of the parent material and on its U/Pb and Th/Pb ratios. Pb isotope ratios can fingerprint different styles of mineralisation within a geological terrain and because these ratios do not change as a result of weathering processes these fingerprints persist into the regolith. Variation in the isotopic composition of Pb as measured in weathered rock, various components of soils and in groundwater thus relate to mixing of Pb from various geological reservoirs including the mineralisation reservoir. Thus it is possible in any of these sample media, and also in associated vegetation, to determine the proportion of Pb that has derived from a high-Pb (mineralised) source or from a high-U source.

HYDROGEOCHEMISTRY - NEW DEVELOPMENTS AND EXPLORATION IMPLICATIONS

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Acid (and saline) groundwaters (commonly down to pH 3), pervasive across the southern Yilgarn Craton, the Gawler Craton and in SE Australia, are commonly believed to be caused by a ‘ferrolysis’ mechanism. Our research suggests an alternative “top-down” mechanism, whereby biochemically mediated reactions, followed by slow infiltration and evapo-transpiration, generate differing soil and groundwater conditions depending on vegetative cover (Figure 1). This new model may have significant implications for use of exploration media such as soil carbonates, interpretation of Au depletion zones (Figure 2), and for the stability of gossans in regolith.

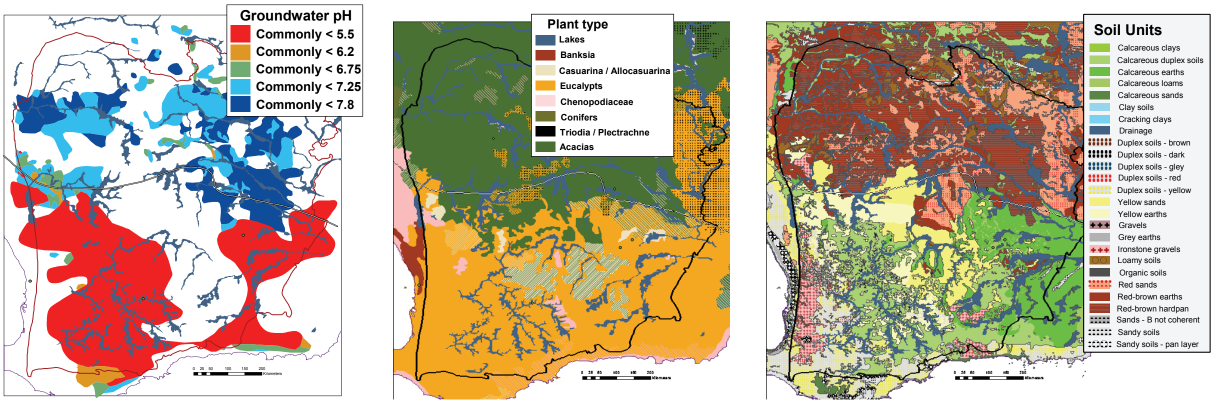

Figure 1: Groundwater pH domains, dominant plant types and soil units for the Yilgarn Craton.

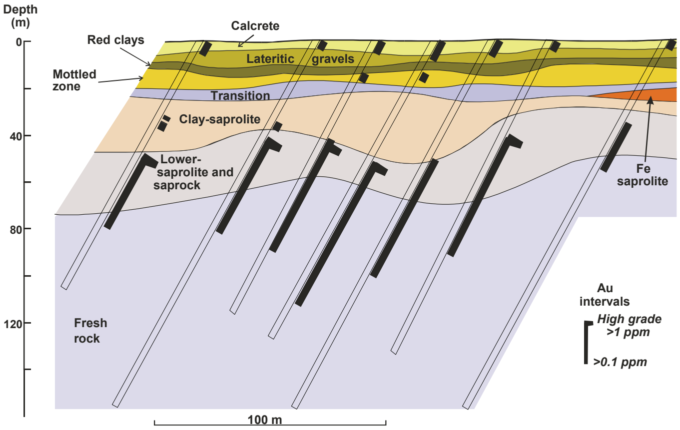

Figure 2: Gold geochemistry at Karari pit (Carosue Dam), indicating depletion throughout the upper regolith, with an enrichment front at the top of the lower saprolite.

In contrast, groundwaters to the north are generally neutral and fresh, though with unusually high NO„ (commonly 50-200 mg/L). Hydrogeochemical exploration for NiS in the NE Yilgarn shows potential for large/greenfields (km’s) and medium (100’s m spacing) scale exploration, and also for smaller scale investigation to assess “near-miss” drilling in brownfields regions. The geochemical halo around Ni deposits is sporadic, although with very few false positives elsewhere. Most high concentrations of metals associated with the Ni hydrogeochemical signature are indicative of sulphides and mineralisation. Chromium is the best indicator element for ultramafic rocks (particularly when S-poor), whereas Ni, Co, Pt and W are the best individual pathfinders for NiS mineralisation.

Hydrogeochemical differentiation and targeting for NiS is improved using the Box-Cox transformation and deriving critical indices from multi-element data. Such indices, consistent with the model for groundwater evolution around weathering sulphides, delineate the sulphide signature independent of the type of water i.e., whether the major parameters of Eh and pH are different. The better performing indices for mineralisation targeting are Miner-S and Miner-FeS that use the mineralised signature (Ni+Co+W+Pt) and take away the groundwater signatures of weathering acid producing sulphides (Mo+Ba+Li+Al) and Fe-rich sulphides (pH-Eh+Fe+Mn) (Figure 3 and Figure 4). Massive NiS certainly gave stronger groundwater signatures than disseminated mineralisation, which commonly were only clearly delineated using these combined indices.

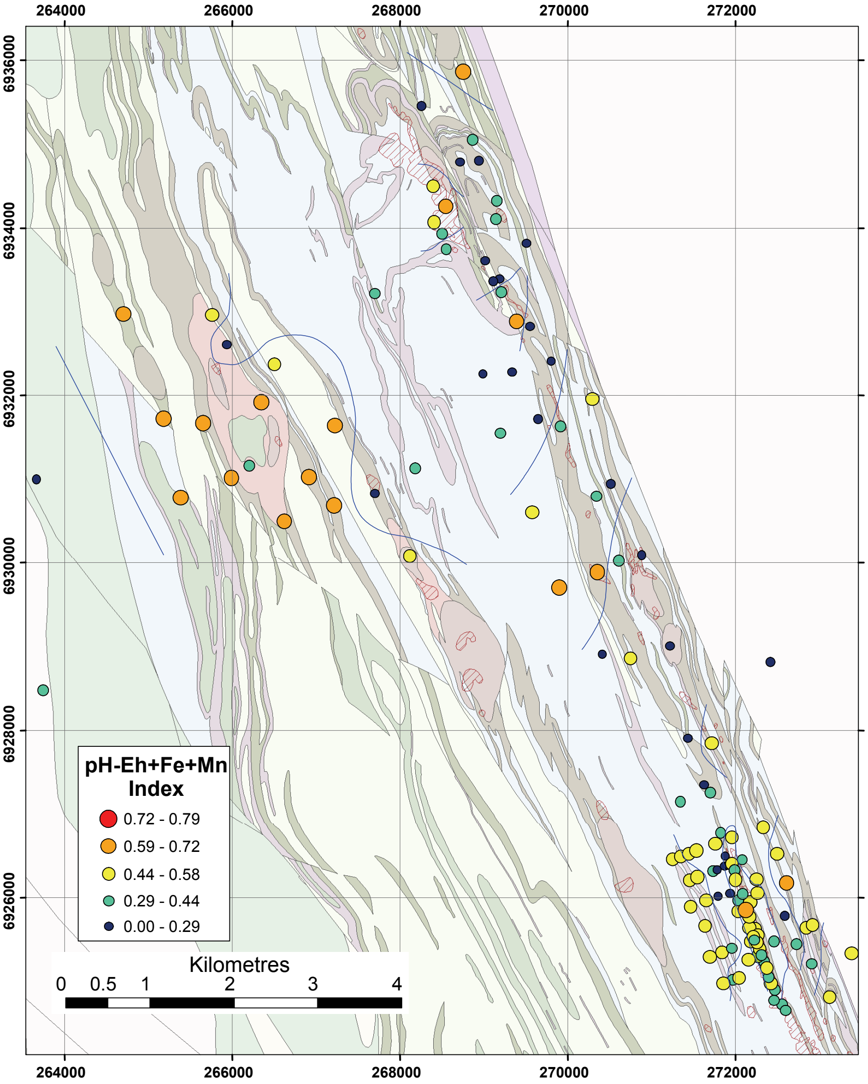

Figure 3: The FeS (pH-Eh+Fe+Mn) index at Camelot (north of Leinster), shows presence of sulphidic systems, particularly (apparently) barren/sub-economic sulphides in the NW of the area

In addition to empirically based indices, we have also modelled groundwater interactions with sulphidic rocks, for both Ni-rich and Fe-rich sulphide systems, with results consistent with our groundwater measurements. In these environments previous weathering means that the sulphide oxidation front is tens of metres below the water table, with extremely limited O_2

access. Modelling within Geochemists Workbench®, has demonstrated that deep sulphide alteration (e.g., pyrrhotite Ý pyrite, pentlandite Ý violarite), can occur with $SOØ^{-}$ as an oxidant and ultimately an additional source of sulphide (presumably mediated by biota):

$$2FeS + 0.4SOØ^{-} + 1.6H_2O \ Ý\ 0.8Fe(OH)_3 + 1.2FeS_2 + 0.8OH^{-}$$

(pyrrhotite) (iron oxide) (pyrite)

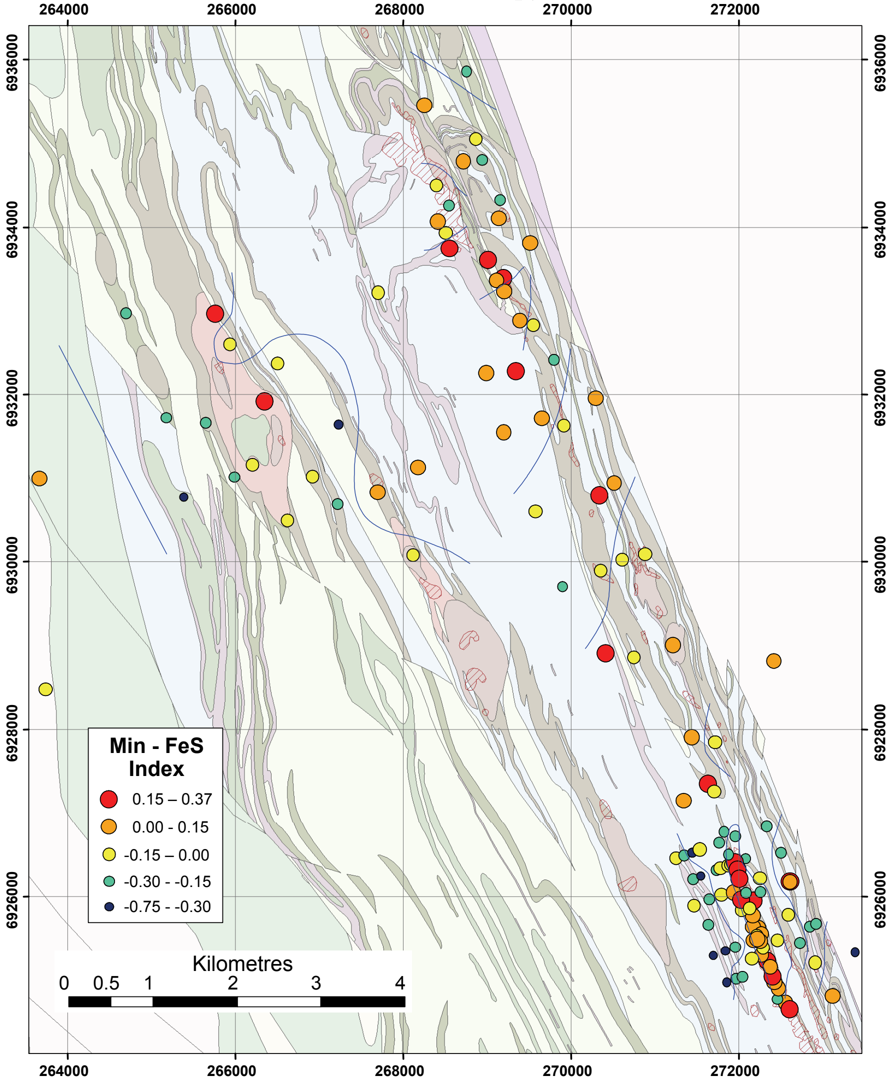

Figure 4: The Min-FeS Index at Camelot. This more strongly indicates the Harmony Ore Body in the SE, and areas of economic NiS intersections in the north of the area.

This results in deep groundwaters contacting sulphides being alkaline and depleted in sulphate, as well as any other potential oxidants such as nitrate (which is probably present in these environments because of prevalent nitrogen fixation around Acacia roots). Modelling also demonstrates that Fe oxides can also be formed as a side product of this conversion, even in anoxic zones (Figure 5). This has implications to our interpretation of the observation of Fe oxides at depth.

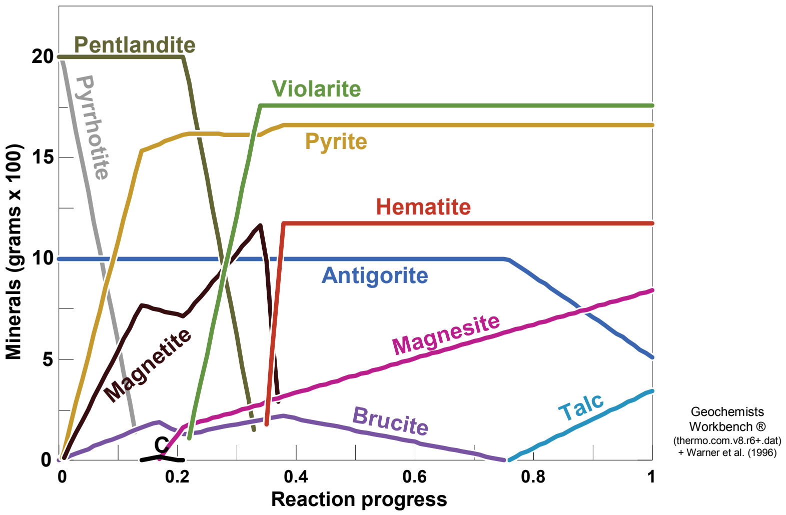

Figure 5: Modelled conversion of primary to secondary sulphides, with additional formation of hematite, with $\mathrm{SOØ}^{-}$ as the oxidant.

In contrast, oxidation of such secondary sulphides to sulphate requires either O_2 or NO„ (as modelled below and in Figure 6):

$2FeS_2$ + 6NO„ + H_2O Ý $Fe_2O_3 + 3N_{2(G)}$ + $4\mathrm{SOØ}^{-}$ + $2H^{+}$
(pyrite) (iron oxide)

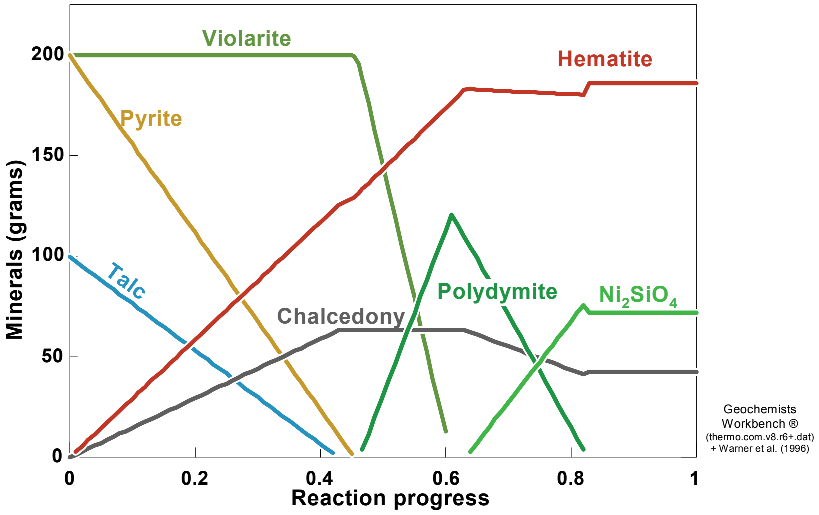

Figure 6: Modelled oxidation of secondary sulphides to sulphate, with nitrate as the oxidant.

Thus, in these environments, shallow groundwaters around sulphides will be nitrate depleted and sulphides enriched and acidic. The degree of acid production is heavily dependant on mineralogy, with Fe-rich systems producing much more acidity than Ni-rich. These predictions for both deep and shallow groundwaters exactly match observations, and provide additional techniques for broad-scale identification of sulphide systems in exploration.

BIOGEOCHEMICAL ACCUMULATION OF TRACE ELEMENTS IN SOILS AND VEGETATION

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Locating ore deposits hidden beneath a transported overburden is an ongoing challenge for the mining industry. In mineralised areas, localised concentration of ore-related elements, relative to background concentrations, occurs in soils through the weathering of parent material. However, if the original land surface has been stripped and an exotic overburden is deposited in its place, the same concentration of trace elements is not necessarily observed in surface soils developed on transported material. Several physico-chemical processes have been suggested to account for the migration of elements into the overburden (Govett 1976; Hamilton 1998; Kelley *et al.* 2006). However, relatively little is known of the effect of biota on the transport of elements from great depths through the regolith, particularly in arid climatic zones. Can plants act as a direct conduit for trace element migration from deep within the regolith to the surface soils?

Analysis of eucalypt tissue from two exploration tenements in Western Australia shows that anomalous concentrations of elements in vegetation samples correlates well with the location of lithological contacts for Au, Cd, U, Th and Co. Elements such as Cu, Zn and Ni in vegetation samples did not show significant correlation with the underlying lithology. Analysis of surface soils (10-25cm) by the Mobile Metal Ion method and by *aqua regia* digest showed similar anomalous responses for the same elements (Au, Cd, U, Th and Co).

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SUPERGENE GOLD FROM SALTY WATER IN THE SOUTHERN YILGARN.

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Natural supergene (secondary) gold deposition is a process whereby chemical weathering of gold deposits can lead to the dissolution of gold from the hypogene primary gold deposit (hosted by sulphides or quartz), transportation in solution and then re-precipitation elsewhere in the weathering profile. Whereas the gold present in the host fresh rock is normally as an Au-Ag alloy (Hough et al., 2007), the secondary gold is usually pure (Lawrance and Griffin, 1994), although secondary Au-Ag alloys have also been shown to form in isolated cases (Webster and Mann, 1984). In the southern areas of Western Australia where groundwaters are highly saline (67,000 mg/L Cl) at up to 3x seawater salinity and acidic (pH from 3 to 7) gold presently occurs in solution as the gold chloride ion and will precipitate in its pure form.

The Golden Virgin pit, Parker Range, south of Southern Cross in Western Australia is a small gold deposit where primary mineralisation occurs as small high grade quartz veins blanketed by up to 30 m of regolith cover. The veins near the base of the pit contain visible primary (Au/Ag) gold in the quartz that occurs closely with masses of iron oxides that are pseudomorphs after sulphides, some remnant sulphides also occur. The gold that now occurs in these iron oxides is likely a remnant of the gold that was once hosted by sulphide. Weathered fracture surfaces in the quartz vein blocks are lined with different generations of secondary iron oxides, clays and sulphates together with an exceptionally rich population of supergene Au crystals. Gold is normally bright in BSE; however the supergene Au at Golden Virgin was also found to contain a population of grains that are darker grey. Upon closer examination it was found that many of these crystals are transparent to the electron beam, with underlying materials visible through them. Some direct analysis of gold crystal edges indicate these so-called nanoplates to be <17 nm thick. SEM observations also reveal complex internal structures to the plates where contouring of the lattice appears to produce these textures and small holes appear to act as seed points. Further examination by TEM confirms these structures are likely to be bend contours related to strain of the lattice, possibly by buckling during settling onto the substrate. On the surface of the gold we have found a separate, nanoparticulate population of gold crystals that are 20-200 nm in crystallite size. These nanoparticles form a band across the gold crystal together with a population of similarly nano-sized halloysite crystals, the band appears like a drying pattern and likely extends beyond the gold crystals on the fracture surface.

This supergene gold occurs closely associated with salt crystals and sometimes intergrown with barite, supporting the premise that native gold (Au/Ag alloy) was dissolved locally into groundwater, the silver remained in solution, and pure gold was precipitated from the saline and slightly acidic groundwater during evaporation. Further confirmation of this was obtained through analysis of the pit water that gave results of 44 ppt Au and 293 ppt Ag. So a higher concentration of Ag in the water despite a lower concentration in the actual primary gold. The single crystal and ultra thin gold plates suggest rapid deposition of supergene gold in this environment, completed on the order of days rather than over prolonged timescales and driven by evaporation. The nanoparticulate fraction of gold would likely have occurred as a colloidal suspension; this represents the first observation of this in nature. Colloidal gold and gold crystals of the dimension reported here are easily transported where nanoparticles could even potentially be carried by gases.

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CALCRETE SAMPLING - TWENTY YEARS ON

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It is twenty years since the discovery of the gold in calcrete association in the Forrestania and Kalgoorlie regions of Western Australia (Lintern, 1989). Following this breakthrough, case studies at numerous Au deposits and prospects showed the association with pedogenic carbonate is widespread and a viable exploration technique was developed to explore semi-arid, "covered" landscapes throughout southern Australia (Lintern and Butt, 1997). Much was made of the discovery of the Challenger Gold Deposit in South Australia (now one million ounce) using calcrete, but many WA mines had earlier had their lives extended due to the success of this technique (Edgecombe, 1997). Calcrete sampling has been used elsewhere, particularly in central Asia and the Americas. In Australia, calcrete sampling for Au continues to be used extensively, particularly in the Gawler and Yilgarn Cratons e.g. Tropicana. A Google search of "calcrete gold" produces about 19000 hits, many linking to company reports. In the past and, increasingly, more recently, (valley) calcrete has been used to find U occurrences.

The Barns Gold Prospect in the Eyre Peninsula, South Australia has become an important site for advances in gold-calcrete research (McEntegart and Schmidt Mumm, 2005; Lintern, 2007; Schmidt Mumm and Reith, 2007). Here, biological, microbiological, luminescence dating, and isotope geochemical applications have given valuable insights on how gold-calcrete anomalies may form. The prospect is located in highly weathered Proterozoic rocks and is overlain by at least 1 m of aeolian quartz sand that thickens to 8 m as a longitudinal sand dune over part of the mineralization. The dune is well-vegetated, with *Melaleuca* shrubs, and *Eucalyptus* trees up to 5 m high. Over mineralization, there are anomalous Au concentrations in plant organs, litter, soils and sand. The highest Au concentrations (9 ppb) occur in calcareous rhizomorphs high up within the dune. Luminescence dating shows that the dune took no longer than 27 000 years to form and mass balance calculations suggest that the Au anomaly in the dune could have formed in less than 10 000 years. Isotope studies at Barns are consistent with earlier work at Challenger and elsewhere and suggest that the Ca is of marine origin. Therefore mineral explorers need not be concerned about whether local weathering of rocks has supplied the Ca or not, since Au anomalies in calcrete can form irrespective of rock type. A biological process, principally involving vegetation, is the most likely mechanism for the Au accumulation in the calcareous sand at Barns.

Based on experiments using samples from Barns, it has been suggested that bacteria may control the precipitation of carbonate and Au due to a pH change through the decomposition of organic molecules such as urea (Schmidt Mumm and Reith, 2007). However, one of the problems with this model is that bacteria are mostly concentrated at the top of the soil profile (where the organic material is located on which they feed) while the Ca and Au precipitation occur deeper in the profile where bacterial populations are only a fraction of what they are at the surface. Furthermore, calcrete is not observed at the dune surface at Barns.

Recent experimental studies on Au uptake by plants indicate that Au nuggets can form in the xylem tissue of plants. Although large concentrations of Au were used in these experiments, it does indicate the propensity for Au to form elemental particles, even in biota. Illuviated phytonuggets may be important as initiation sites for Au to nucleate in the soil or carbonate profile.

Since the early years of discovery there has been few technical breakthroughs and our knowledge of the "how, why and where" of the gold-calcrete association has not readily advanced. In recent years, however, increasing effort by researchers has been placed on geochemical process and, as a result, we now have a better understanding of gold-calcrete anomalies; as to whether this new knowledge will lead to more discoveries remains to be seen. Calcrete sampling, like any other successful surficial sampling technique, will continue to be used. Advances of our understanding of the technique to assist explorers will be incremental and may relate to landform studies and modelling paleogeomorphological surfaces.

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DEVELOPMENTS IN THE AUTOMATED INTERPRETATION OF REGOLITH SPECTRA

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Abstract not available.

THE MINERALS DOWN UNDER NATIONAL RESEARCH FLAGSHIP

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Flagships

The National Research Flagship program was initiated in 2003 by CSIRO to address Australia's major national challenges through multi-disciplinary research partnerships using capabilities from across CSIRO and working with other research organisations as well as industry. Total investment up until the 2010-2011 FY is expected to be $1.5 billion. The first group of 6 Flagships established in 2003 were:

- Food Futures
- Light Metals
- Preventative Health
- Water for a Healthy Country
- Wealth from Oceans
- Energy Transformed

On the basis of the success of these initiatives and on the need to broaden the scope of the Flagships, CSIRO went to government in the first half 2007 with propositions for a further 3 Flagships which have now been successfully funded. These are:

- Minerals Down Under
- Climate Adaptation
- Niche Manufacturing

Minerals Down Under

This Flagship is developing projects from across the minerals value chain from exploration through mining to mineral processing that will have the greatest impact on enhancing wealth to Australia. It will involve the collaboration of 9 CSIRO divisions, universities, government organisations such as ANSTO, other scientific bodies such as Geoscience Australia and the State and Territory Geological Surveys. There are four research areas, called "Streams" which have direct application to mineral exploration. These are:

Mineral System Life Cycles and Targeting This Stream will build on the success and capabilities of CRC LEME and pmd*CRC and focus on understanding the formation and weathering of ore systems of importance to Australia. Deliverables will include new technologies and techniques for increased exploration success and a toolkit of advanced computational modelling capabilities able to simulate ore-related processes at all scales.

Terrain Scale Technology Applications Research here will focus on the provision of data infrastructure and new types of data and expertise to government agencies. It will leverage strategic research first initiated under the banner of Glass Earth, that saw the development of the Solid Earth and Environment Grid (SEEGrid), the current AuScope Grid, the initiatives in automated logging technologies (HyLogging) to create Virtual Core Libraries and the use of space and airborne hyperspectral surveys to deliver the next generation of mineral maps.

3D Mapping Technologies This stream has as its goal that Australian geoscientists will operate consistently in 3D by 2025 through development of new software for efficient interpretation of existing data types and new geophysical tools for defining 3D geology. The deliverables will be a toolkit of computational techniques for the fast production of 3D geological maps, new inversion techniques combining multiple geophysical and geological datasets and a new tensor gradient airborne magnetometer system (GETMAG).

Enhanced Knowledge from Drilling The aim will be to reduce the cost of drilling and enhance the quantity of information obtained from boreholes through the design, testing and delivery of effective drilling and down-hole data acquisition technologies. The research will have application to both exploration and mining.