SAMPLE MEDIA

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GOSSANS AND IRONSTONES

DEFINITION

A *gossan* is the weathered expression of a rock that contains substantial amounts of sulphide mineralization; it is, in effect, a saprolite developed over bodies of massive or matrix sulphides. A massive sulphide body consists almost entirely of sulphide minerals; matrix or 'mesh-textured' sulphide bodies consist of a continuous matrix of sulphides containing isolated non-sulphide minerals, mostly silicates. Gossans *sensu stricto* do not form from disseminated sulphide bodies. The term has no economic connotation and may be applied to the weathered product of any sulphide, including barren pyrite. Gossans derived from Fe-rich sulphide assemblages typically consist largely of Fe oxides, whereas gossans formed from the weathering of Fe-poor sulphides (*e.g.,* carbonate hosted Pb-Zn sulphides) may be siliceous or have high Mn contents. The following terms have been applied to gossans:

- *Direct gossan* (syn. *indigenous*): formed *in situ.*
- *Fertile gossan*: formed by weathering of sulphides (commonly of base metals) of potential economic significance.
- *Fossil gossan*: formed during an earlier weathering episode; particularly applies to gossans buried by later sedimentary or volcanic events.
- *Solution-deposited gossan* (syn. *leakage gossan*): an accumulation of hydromorphically transported Fe oxides derived from a sulphide source. It may occur within a gossan profile or some distance away.
- *Translocated gossan*: gossan that has been mechanically moved. Subsequently, it may have been recemented.
- *Barren gossan:* formed by weathering of Fe sulphides containing no elements of economic significance (commonly refers to base metals).

Ironstone is a general term that describes any highly ferruginous weathered outcrop, including gossans. Ironstones may or may not be derived from sulphides, but gossans are all derived from sulphides. Because it is commonly not possible to recognize a gossan in hand specimen, it is better to refer to any very ferruginous field sample as an "ironstone" until definite evidence of a sulphide parent is obtained by petrographic or geochemical study, or by drilling. Ironstones with a fabric and/or composition suggestive of a gossan, but not developed over sulphides, are referred to as *false gossans* or *pseudo-gossans.*

Historically, early metal production was from native Ag, Au and Cu, or secondary minerals formed by oxidation of massive sulphides. The distinctive colours of secondary Cu minerals (*e.g.,* malachite and azurite) attracted early miners to gossanous outcrops. Secondary Cu minerals were processed at Rio Tinto, Spain during the third or fourth millenium B.C., with jarosite being processed to recover Ag as early as 1200 BC. The ferruginous outcrops in Cornwall were producing Cu and Sn by 400 BC and gave rise to the term gossan to describe 'a kind of imperfect iron ore, commonly of a tender rotten substance, and red or rusty iron in colour' (Taylor and Thornber, 1992).

During the early 20th century, considerable work was done in the USA and Australia to describe the diagnostic textures (fabrics) and boxworks of gossans, to distinguish them from other ferruginous outcrops *(e.g.,* Blanchard, 1939, 1968). A more recent review is given by Blain and Andrew (1977). However, not all gossans have sufficiently well-developed textures for such a distinction to be made, so that geochemical discrimination has been used instead, with the advantage that it also tends to be less costly. The geochemistry of ironstones and gossans has subsequently been widely used in Australia since the 1970s in exploration for Ni and other base metals.

DISTRIBUTION

Gossans have formed on sulphide mineralization throughout Australia, under a wide variety of climatic and geomorphological conditions. They are generally best developed in regions that have been deeply weathered. Where there is little or no weathering, outcropping gossans are immature, commonly containing relict primary sulphides or secondary oxidate minerals (*e.g.,* Halls Peak; *this volume*).

It is generally assumed that sulphide oxidation and leaching, resulting in gossan formation, are most active in humid, warm to tropical seasonal climates, similar to those that prevailed over much of Australia in the past and still occur in parts of the Northern Territory and Queensland. However, most gossans have been discovered in semi-arid to arid regions, generally in eroded areas of moderate outcrop of saprolite or fresh rocks. In savannas and rainforests, the Fe from sulphides may remain in solution as organic complexes, or dissolve from secondary oxides high in the profile, to appear in ferrallitic soils on the wall rocks, rather than form gossans that later become indurated. Accordingly, gossans may be poorly developed or absent in the upper parts of deeply weathered profiles, even in arid climates (Butt, 1995). There is little direct evidence that gossans will not occur in such sites, but none appear to have been described to date. Some general observations: -

- In erosional areas, gossans vary from large ferruginous masses to discontinuous outcrop or even float, commonly in a zone with thin soil and lag. Many appear quite insignificant, suggesting considerable degradation during their evolution.
- Gossans with well-developed zoned profiles may occur even in terrains where the pre-existing deep weathering profile on the wall rocks has been largely stripped, *e.g.*, at Kambalda. This implies that much of the sulphide oxidation may post-date erosion and be due to ongoing weathering under arid conditions. Certainly, the oxidate assemblage of carbonates and sulphates is consistent with formation under such an environment, so it is possible that only the upper part of the oxide zone relates to an earlier weathering phase.
- Poor development and/or preservation of gossans may be anticipated in areas that were topographically low during humid climatic periods. Many of these are still in lower parts of the landscape, buried by colluvium and alluvium, and may have remained wet or waterlogged. Even where topographic inversion has occurred, preservation of much of the regolith profile would mean that there would be little or no gossan, at least in upper horizons.

FORMATION OF GOSSANS AND IRONSTONES

Gossans

Weathering of sulphides involves dissolution and oxidation of S and most other constituent elements, especially Fe, the precipitation of secondary minerals and, commonly, further recrystallization and dehydration. Silicates derived from the weathering of wallrocks or gangue minerals are also commonly present. These processes involve changes in physical conditions, such as increases in pH and Eh. The great depth of oxidation of some massive sulphide deposits, some extending to 100 m or more below the water-table on Ni sulphide deposits in the Yilgarn Craton, has been explained as being due to electrochemical processes (Thornber, 1972; Thornber and Taylor, 1992). In this model, the upper part of the sulphide body, near the water-table, becomes a cathode where oxygen and water are reduced to hydroxyl ions. This process requires an input of electrons, as illustrated by the general reaction:

$$O_2 + 2H_2O + 4e^- \Rightarrow 4(OH)^-$$

The electrons required for this reaction are generated at depth – the anodic region of the sulphide body – by oxidation of sulphides, commonly Fe sulphides:

$$FeS_2 + 8H_2O \Rightarrow Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^-$$

Electrons are conducted by the sulphide body to the cathodic region.

The anodic reactions, and the subsequent oxidation and hydrolysis of ferrous iron, generate considerable acidity:

$$4Fe^{2+} + O_2 + 6H_2O \Rightarrow 4FeOOH + 8H^+$$

Thus, the environment of sulphide weathering and gossan formation commonly has a very low pH. However, this may be buffered by wallrocks, *e.g.*, limestones adjacent to Mississippi Valley-type Pb-Zn deposits, and serpentine and carbonates of the gangue and wallrocks of massive and, especially, matrix Ni sulphide deposits.

In a 'typical' gossan profile, a supergene enriched zone may occur above the weathering sulphides, and be overlain by successive zones of sulphates, carbonates and phosphates, before giving way to the Fe oxide phases that dominate the outcropping gossan (Figure 1A). However, given their high solubility, the carbonates, sulphates and other oxidate minerals probably formed predominantly under arid conditions, as noted above.

Of the many cations that are released by sulphide weathering, Fe is the most abundant, so Fe hydroxides and oxyhydroxides are major precipitates. Other cations either co-precipitate with the Fe phases or are adsorbed onto their surfaces. Recrystallization/dehydration of the Fe-rich precipitates may expel foreign cations to form their own discrete minerals, although studies of Fe oxide minerals in gossans from NW Queensland show that high concentrations of base metals can be retained in goethite and hematite within gossan profiles (Scott, 1986). Alunite-jarosite minerals can also host chalcophile elements in gossans (Scott, 1987). They have the general formula: -

$$AB\,(XO_4)_2(OH)_6$$

where A= K, Pb, Ca, Ag, Ba, Sr and REE; B=A1 or Fe with minor Cu and Zn; and XO_4 is predominantly SO_4^{2-}, PO_4^{3-}, but can also include AsO_4^{3-} and SbO_4^{3-}.

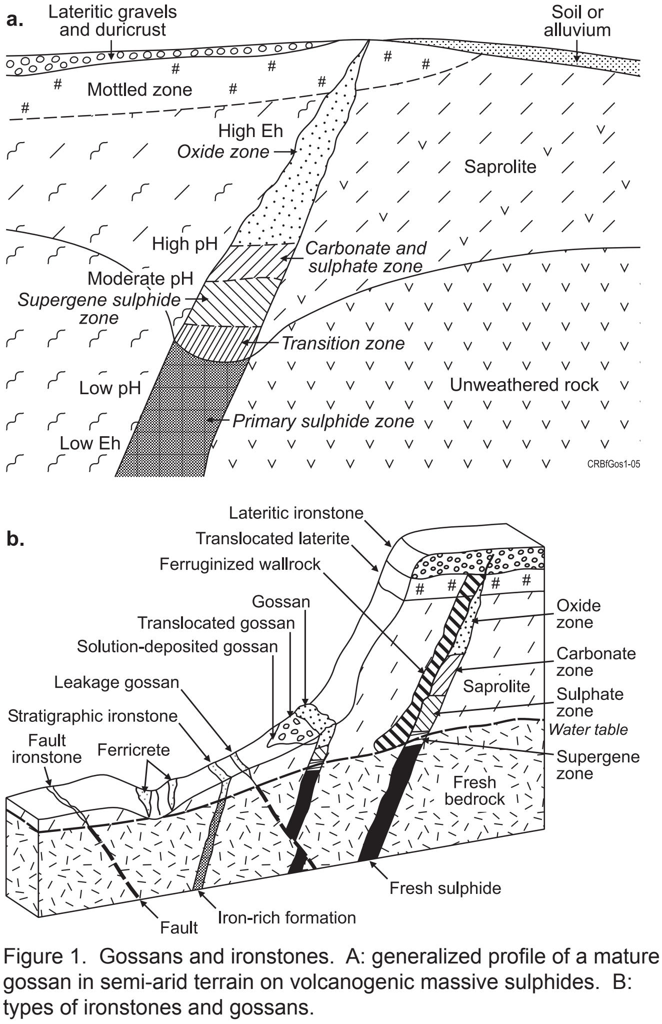

Figure 1. Gossans and ironstones. A: generalized profile of a mature gossan in semi-arid terrain on volcanogenic massive sulphides. B: types of ironstones and gossans.

Carbonates and ferromagnesian silicates, such as chlorite, amphiboles, biotite, olivine and serpentine, commonly occur as gangue in ores. Carbonates are very susceptible to weathering, and dissolve under the acid conditions of oxidizing sulphides. The silicates ultimately break down to Fe oxides, kaolinite and silica (Table 1). In comparison, quartz and a variety of accessory minerals such as rutile, cassiterite, garnet, xenotime, monazite, tourmaline and spinels (*e.g.,* gahnite, chromite) are generally resistant to weathering and are retained in gossans and associated soil.

TABLE 1

WEATHERING PRODUCTS OF SOME COMMON ROCK-FORMING SILICATES

Olivine	=>	Fe oxide + Silica
Plagioclase	=>	Kaolinite
K-feldspar	=>	Illite => Kaolinite
Amphibole	=>	Fe oxide + Kaolinite
Chlorite	=>	Fe oxide + Kaolinite
Biotite	=>	Fe oxide + Kaolinite

Ironstones

There is a wide variety of ironstones in deeply weathered terrain, many of which may resemble gossans in field occurrence and composition (Figure 1B). Most ironstones consist of goethite and hematite, with minor quartz and other silicates, but have diverse mechanisms of formation. Some ironstones are essentially linear in outcrop, following an underlying geological unit or structure. *Stratigraphic* ironstones are largely residual accumulations on Fe-rich lithologies, such as Fe-rich carbonates (Taylor, 1973). Ironstones along *faults*, *lithological contacts*, *bedding planes* and other channelways are formed by precipitation of Fe, derived from weathering of country rocks, in these more oxidizing zones of water flow. All these ironstones may resemble gossans, and may have concentrated one or more base metals (*e.g.,* Killara Cu pseudogossan; *this volume*). Fault ironstones can contain a high proportion of quartz breccia. Siliceous or ferruginous boxworks after primary or secondary minerals such as carbonates, garnet or olivine may superficially resemble sulphide boxworks. Strongly jointed and textured rocks also give rise to similar cellular structures.

Other ironstones may be more-or-less conformable with the landsurface, as an horizon in the regolith. Examples include *lateritic duricrusts*, either at surface or buried beneath transported overburden and *ferruginous pans,* precipitated at the level of past water-tables or redox-fronts; in each of these, original rock fabrics may be partly preserved or completely destroyed. *Ferricretes* and *seepage ironstones* have formed by the precipitation of Fe oxides (and, in places, Mn oxides) at breaks of slope, swamps and along watercourses. Botryoidal, cellular, pisolitic and nodular structures are common in lateritic duricrusts and ferricretes.

USE AS SAMPLE MEDIA

Procedures

Many of the major sulphide ore deposits of Australia (*e.g.,* Broken Hill, Mt Lyell, Mt Morgan, Mt Isa and Kambalda) were found by recognition of outcropping gossans (Taylor *et al.,* 1980). However, today recognition of gossanous material is more likely to be needed when drilling through transported overburden. Nevertheless, the features needed to distinguish gossans from ironstones are similar for both outcropping and buried gossans and, since the 1970s, multielement geochemistry has been successfully employed for this purpose. This involves using pathfinder element abundances to screen ferruginous samples, whether or not these have boxworks or other gossanous textures, or even if target element concentrations are not anomalous.

Because the formation of gossans commonly involves multiple events during an extended period, leading to variable amounts of ferruginization, silicification and calcification, individual samples are chemically highly variable. Thus, it is desirable to collect a number of discrete samples from each occurrence to fully evaluate it (N.B., more information is gained from a group of individually analysed samples than from bulking the samples prior to analysis). However, in many cases where the ferruginous material is obtained by drilling, multiple samples may not be available and identification of the material as a gossan must rely on comparison with known gossans in the area and determining whether the composition could have a sulphide source.

Once an ironstone has been identified as a gossan, attempting to determine whether the sulphides from which it is derived are likely to be economic is difficult because the composition of the gossan does not necessarily reflect that of the parent sulphides. For example, Zn may be highly depleted (*e.g.*, at Mt Isa, *this volume*) and Au can be enriched (Scott *et al*., 2001) during gossan formation. Thus, a thorough understanding of the weathering processes and any influence of the wall rocks is needed before attempting a prediction with confidence.

Multielement geochemistry

Analysis for target elements alone is commonly inadequate for correct identification of gossans, either because these may be leached from true gossans or, conversely, concentrated in ironstones with no sulphide precursor. Specific pathfinder elements or suites of elements may be diagnostic. For example, Cu-rich ironstones are common, but most are unrelated to mineralization and lack associated pathfinder elements; examples include the Cu-rich ironstone on a shale-dolerite contact (Killara pseudogossan; *this volume*), anomalous Cu in stratigraphic ironstones (Taylor, 1973) and Cu in fault ironstones (even when partially derived from weathering sulphides: Bampton *et al.,* 1977). Conversely, the presence of As is a good indicator of the significance of Cu anomalies, because it is derived from pyrite associated with the Cu mineralization (Glasson, 1973; Taylor, 1973). General multi-element suites for various mineralization types (Taylor and Thornber, 1992) are given in Table 2.

The geochemical data are best analysed using multivariate statistical techniques. These are more effective if the variables have normal distributions and, depending on the distribution of each element, log or power transformations may be needed. Well-characterized reference data sets are required, representing the principal types of gossans and other ironstones in the survey area, based upon major and trace element data. Some of most effective procedures include stepwise discriminant analysis (*e.g.*, Taylor and Scott, 1982) and canonical variate analysis (*e.g.*, Smith *et al.,* 1983). In the latter study, reference sets of Cu-Zn-Pb gossans, pseudo-gossans (i.e., ironstones with anomalous geochemical compositions) and a background ironstone group, all from Western Australia, were used, based on 13 elements. A plot of the first two canonical variates, dominated by only seven of these elements, gave a marked separation of the group means, with very little overlap of individual samples (Figure 2). This reference plot was then used to allocate unknowns. Of six sets of unknown ironstones, four were allocated correctly, one required further field evaluation and one (barren gossans) was incorrectly classified because of the absence of an appropriate reference group. Thus, the success of these procedures depends on the existence of diagnostic element suites and the availability of suitable reference samples, preferably from the search region.

TABLE 2
ELEMENT SUITES FOR GOSSAN IDENTIFICATION

Host Rocks	Target mineralization	Elements
Mafic-ultramafic volcanics	Ni-Cu	Ni, Cu, Co, Pt, Pd, Ir, Se, Te (Cr), (Mn), (Zn)
Felsic volcanics	VMS	Cu, Pb, Ag, Au, As, Sb, Bi, Se, Hg, Sn, Ba
	Cu-Mo-Au	Cu, Mo, Au, Re
Sediments	Pb-Zn-Ag	Pb, Zn, Ag, Cu, As, Hg, Sb (Mn), (Ba), (Co), (Ni)
	Cu	Cu, As, Pb, Sb, Ag, Hg (Mn), (Zn), (Co), (Ni)
Carbonates	Pb-Zn	Pb, Zn, Cd
Skarns	Cu-Zn, Pb-Zn Sn, W, Au-Ag	Cu, Pb, Zn, Sn, W, Au, Ag, Mn, Ca

After Taylor and Thornber (1992)
Elements in parentheses are negative indicators.
Al, Si, Cr, V, Ti, Mn and P are also generally negative indicators, being enriched in lateritic ironstones.

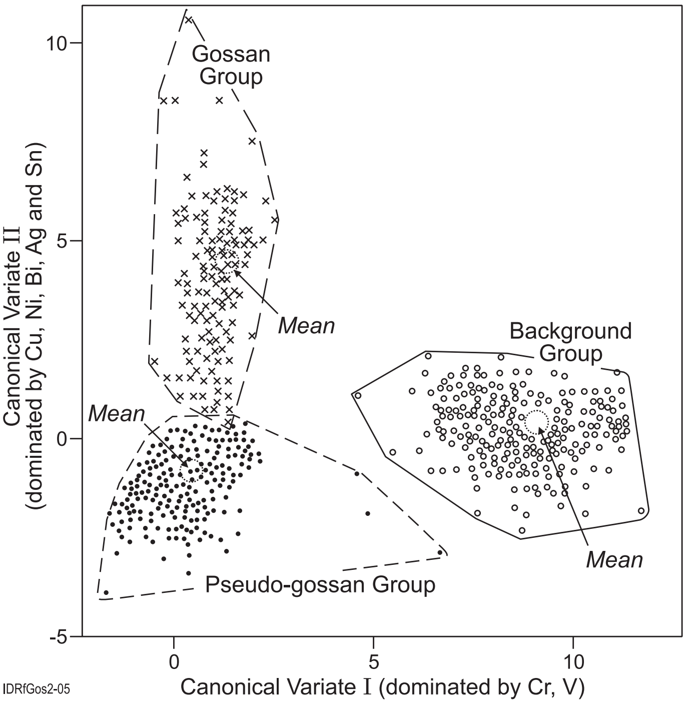

Figure 2. Plot of canonical variates I and II for gossans, pseudogossans and ironstones from Western Australia, showing separation of the three groups (after Smith et al., 1983).

Group separation is difficult to achieve in the case of Ni sulphide exploration. Gossans derived from Ni sulphides have similar Ni contents to gossans on pyritic sulphides in associated sediments, and to a variety of ironstones developed on barren ultramafic rocks. The latter represent a significant source of Ni as silicates. Only Cu and the platinum group elements (PGE) are consistently associated with Ni sulphide mineralization and have potential as exploration pathfinders. Due to differential leaching and some redistribution during weathering, gossans over massive sulphides generally have Ni:Cu ratios of 2-6:1, compared to 10:1 in the sulphides themselves. However, as the various other types of ironstones may have similar abundances and ratios, it is not possible to use these elements alone to identify gossans. The PGEs, especially Ir, show little mobility during weathering, hence high concentrations in ironstones has considerable significance, both for massive/matrix sulphides (Travis *et al.,* 1976; Moeskops, 1977) and disseminated sulphides (Mt Keith Ni sulphide deposit; *this volume*). However, there are few data from more recently developed analytical techniques.

Past gossan evaluation relied on other elements and their relative abundances in the other ironstones. Nickel sulphide gossans have low Mn and Cr, and very low Zn and Pb contents; lateritic ironstones on ultramafic rocks have high Ni and Cr, medium to low Mn, and low Cu, Zn and Pb contents; ironstones and barren gossans developed on sulphidic shales have high to medium Ni, Zn and Mn contents, with medium Cu and Cr, and low Pb. Discriminant analysis by Bull and Mazzucchelli (1975), based on Ni, Cu, Co, Cr and Mn data, correctly classified about 90% of 270 samples as either Ni gossans or other gossans and ironstones. A principal component analysis by Joyce and Clema (1974) found that the first principal component (Cu+Ni) accounted for 41.6% of the variance and is related to massive Ni-Cu gossans; the second principal component (Cr, Zn and Mn), 25.9% of the variance, is related to lateritic ironstones; the third principal component (positive Zn, Cu, Mn and negative Pb, Ni and Cr), 14.6% of the variance, is unexplained. Clema and Stevens-Hoare (1973)

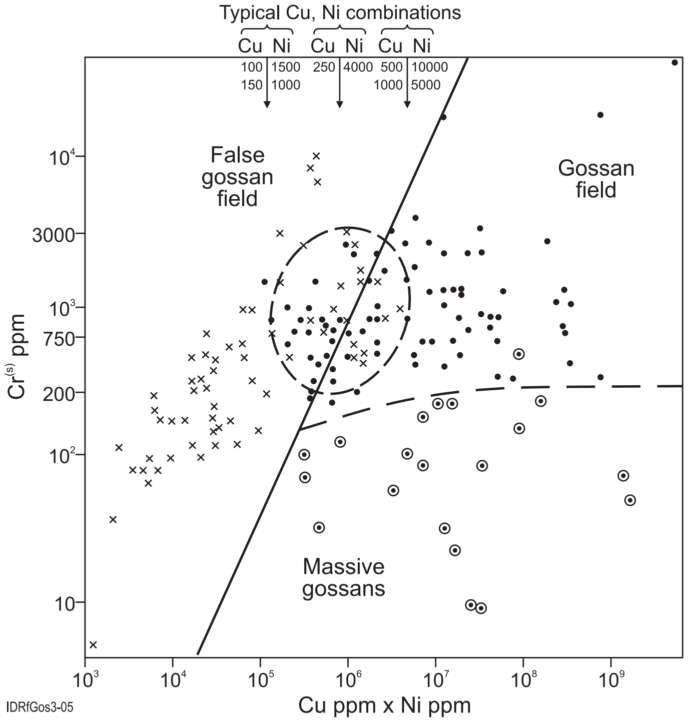

Figure 3. Gossan discrimination diagram (Joyce and Clema, 1974), indicating area of uncertainty due to overlapping compositions (after Moeskops, 1977).

and Joyce and Clema (1974) developed simple graphical procedures based on this statistical analysis, which correctly classified about 95% of 400 samples as either Ni gossans or other gossans and ironstones. Using new data, Moeskops (1977), similarly showed 80-90% successful discrimination using these procedures, and recommended analysis for Cu, Ni, Cr, Mn, Zn and Pb (where Cr is that dissolved by a nitric perchloric acid digestion). Nevertheless, an overlap in compositions remains (Figure 3) and he concluded that this could only be resolved by determining PGE and Se contents.

Lead isotope ratios

Positive identification of gossans may also be made with Pb isotopic ratios, due to the differences in isotopic signatures of country rocks, barren sulphides and potentially economic mineralization. Variations in Pb isotopic ratios are due to: -

- Radioactive decay of U and Th;
- Differences in initial U/Pb and Th/Pb ratios and
- Mixing of Pb evolved in different environments.

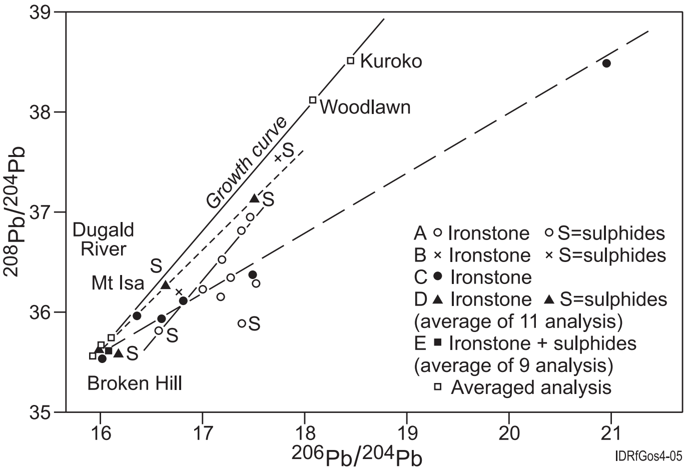

Figure 4. Lead isotope ratio plot for ironstones and underlying sulphides from northwest Queensland compared with other Proterozoic base metal deposits (after Gulson and Mizon, 1979).

Separation of Pb from U and Th to form an orebody at a particular time gives it a unique signature of $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ isotopic ratios. In Pb-rich deposits, the signature is homogeneous and does not change appreciably after formation, due to the high initial Pb/Th and Pb/U ratios. However, in Pb-poor orebodies, the isotopic ratios are not homogeneous and change with time, due to the formation of radiogenic Pb. The ratios may also vary markedly within the deposit, because of variations in initial U/Pb and Th/Pb ratios. The isotopic signatures are not influenced by weathering.

Isotopic studies of numerous sulphide deposits and their gossans have shown that individual metallogenic provinces have distinctive signatures. These signatures are significantly different from those of gossans and ironstones formed on barren Fe sulphide deposits and other Fe-rich lithologies. These barren ironstones contain Pb and other base metals derived from a variety of sources during weathering and have a random Pb isotope signature. Gulson (1986) claimed a success rate of 80% for the classification of gossans and ironstones with low base metal potential, including recognition of the Killara Cu pseudogossan (*this volume*), from gossans on mineralization in the Mt Isa district (Figure 4).

WEATHERED BEDROCK: SAPROLITE AND SAPROCK

DEFINITION

Weathered bedrock is a general term that refers to rock that has been chemically altered but is still coherent, with original structural characteristics and/or fabric preserved. It is equivalent to saprolith, and comprises two units, saprock and saprolite (Figure 5). Saprock is a compact, slightly weathered rock with low porosity, defined as having less than 20% weatherable minerals altered. Weathering effects are mainly at contacts between minerals and intramineral fissures, along shears and fractures through the rock as a whole, or affecting only a few mineral grains or mineral species. The upper boundary of saprock may be difficult to locate precisely. Saprolite is weathered bedrock in which more than 20% of weatherable minerals have been altered but in which the original fabric of the parent rock, originally expressed by the arrangement of the primary minerals (*e.g.*, crystals, grains), is retained. The term may be extended to include regolith materials in which only larger structures such as bedding, schistosity, veining or lithological contacts are preserved. These features imply that weathering has been isovolumetric, pseudomorphic and *in situ*, with negligible vertical (collapse) or lateral physical movement.

FORMATION AND DISTRIBUTION

The chemical alteration responsible for the transformation of bedrock to saprolite includes: -

- Leaching of soluble alkalis, alkaline earths and some transition metals from less stable minerals (sulphides, carbonates, ferromagnesian minerals and alumino-silicates such as feldspar) by groundwater, transforming them to stable secondary minerals, principally clays and Fe oxides. Resistant minerals (quartz, heavy minerals) are retained and less soluble constituents (Ba, Ti, Cr, Zr) are relatively enriched.
- Precipitation, in specific environments, of silica, Fe oxides and Ca-Mg carbonates as absolute enrichments.

Through these processes, primary minerals are pseudomorphically replaced and the precipitated oxides and carbonates form cements that preserve rock fabrics. The principal secondary minerals of the saprolite are Fe oxides, kaolinite and smectite. Uncemented saprolite is mostly soft, especially towards the top, where it may become increasingly clay rich. It has a wide range of colours: green, grey, yellow, brown, red and black. When pale grey or white, it is commonly referred to as ‘pallid zone’.

Weathered bedrock or saprolith is the dominant unit of deeply weathered regoliths and can be >30 m thick. In lateritic profiles, further weathering of saprolite forms mottled and plasmic clays and lateritic residuum. In areas where these latter horizons either did not form or have been eroded, saprolite or saprock may either outcrop or be obscured by

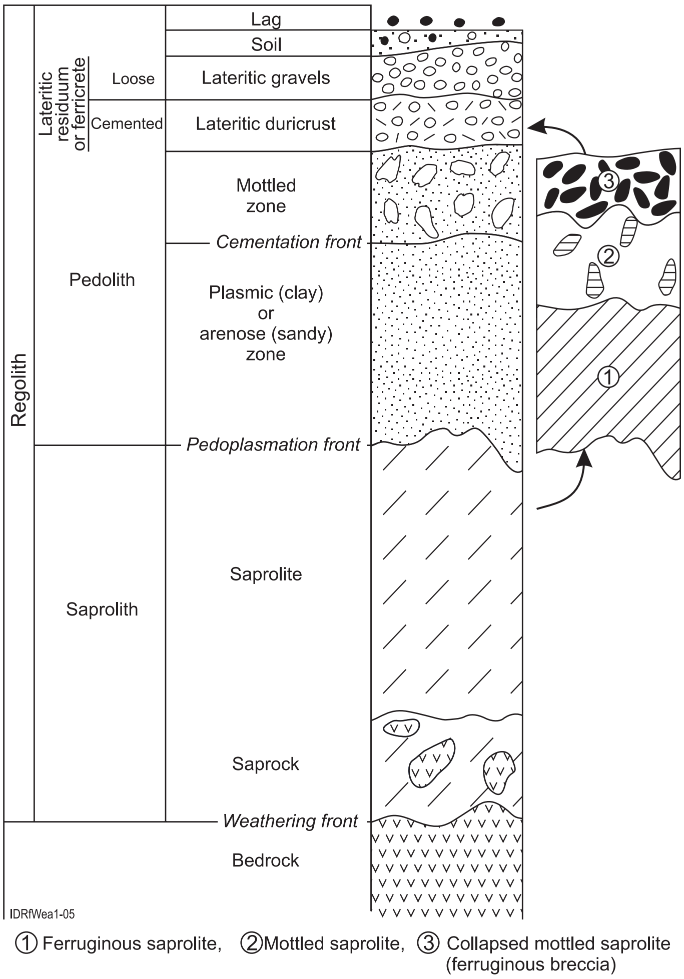

Figure 5. A generalised regolith profile (after Anand et al., 2002).

residual soils or transported overburden. Saprolite and saprock are widespread across continental Australia and parts of Tasmania. They are best preserved in semi-arid to arid regions, especially where there is low relief and disconnected drainage. Here, they are protected from erosion and capped by ferruginous, siliceous or calcareous duricrust or transported overburden. They are less well preserved in areas of high relief, such as much of the Eastern Uplands and inland hill and mountain ranges. Nevertheless, remnants of a former, more widespread deep regolith remain in these areas. Weathering and hence saprolite formation continue, even in arid regions, but are more active in humid climates, especially in the tropical north of Australia.

USE AS A SAMPLING MEDIUM

Saprolite is probably the most commonly used sample medium, particularly at the prospect scale, and for brown-fields exploration. It replaces lithogeochemical sampling where fresh rocks are concealed, and soil sampling where soils are poorly developed or partly transported. Geochemical anomalies in saprolite are dominantly residual, but hydromorphic dispersion haloes have been recorded for some elements, *e.g.*, Pb in some semi-arid and dry savanna environments (*e.g.*, Teutonic Bore, WA: Greig, 1983; Butt, 1992; Woodcutters, NT: Taube, 1978). Multi-element dispersion has been noted at Thalanga (Granier *et al.,* 1989) and Osborne (Lawrance, 1999; also *this volume*) although, at these sites, dispersion is associated mainly with unconformities and overlying sediments. The expected target size for a given ore deposit type depends largely upon the chemical mobility of the elements under deep weathering and subsequent, commonly arid, episodes. In general, the less mobile the element and the deeper (i.e., the nearer to fresh rock) the sample is taken, the smaller the anomaly size. Of the usual indicator elements, those immobilized in Fe oxides, clay minerals or stable secondary minerals (Cu, Mo, As, Sb and Pb) form strong anomalies in saprolite derived from mineralized rocks. Conversely, weathering can leach mobile elements such as Zn almost entirely, especially from the near-surface (Teutonic Bore: Greig, 1983; Butt, 1992), so that the detectable anomaly is again restricted. Primary alteration haloes are preserved if the elements are held in resistant minerals such as rutile, tourmaline, muscovite or barite (*e.g.*, Scott *et al.,* 1994). Secondary enrichment of target metals, derived largely from bedrock with only background abundances (whether hosted by silicates or minor sulphides), may give false anomalies, for example concentration of Cu along faults and contacts (Killara: *this volume*) and of olivine-derived Ni over ultramafic rocks. Such enrichment may, however, become secondary mineralization in its own right, importantly including bauxite, Ni+Co laterite and some Mn deposits; supergene Au and Cu deposits are also enrichments in saprolite, developed over primary mineralization that itself may be sub-economic.

SAMPLING PROCEDURES

Outcropping saprolite can be chip-sampled as an adjunct to gossan, ironstone or laterite sampling. However, as a survey technique, this is liable to bias, since only the most resistant or secondarily hardened rocks are exposed, and these may not be representative of the unexposed rocks. Trenching (costeaning), if logistically possible, is useful for local investigations where the saprolite is soft. Elsewhere, drilling is used.

Rotary air blast (RAB), reverse-circulation blade, roller, percussion, or air-core drilling are routinely used for saprolite sampling. Auger drilling can be used to sample the upper saprolite, generally only within about 5-15 m of the surface, although this may not be possible where there is strong induration (ferruginous, siliceous or calcareous duricrusts), or where the surface horizons are very wet. A number of strategies can be adopted. These include drilling: (i) to a set depth, to fresh bedrock and/or until the drill cannot penetrate farther; (ii) until ‘recognizable saprolite’ is visible in the cuttings; (iii) in areas of deep transported overburden, to base of the overburden and collecting either an ‘interface sample’ across the unconformity (Quasar: *this volume*; Interface, *this volume*) or to the uppermost *in situ* material, whether having recognizable rock fabrics or not.

The drill spacing is critical, especially where little or no secondary dispersion into saprolite is expected. Where samples are collected deep in the saprolite, dispersion may be so restricted that the anomaly is of much the same width as the primary mineralization itself. For narrow targets, such as massive sulphide lenses, where there is little lateral dispersion, vertical drilling on centres of 10 or even 5 m across strike is commonly used. Rather wider intervals may be adequate if overlapping angle drilling is used, but care must be taken to allow for the effects of strong leaching, depletion, and, potentially, transported overburden.

Samples obtained by these methods are generally composites of cuttings from 1-2 m intervals. It is best if the cuttings are passed through a cyclone, to minimize dust-loss, and collected either into plastic bags or into spoil heaps on the ground. Wet samples are collected in calico bags, although these may leak (*e.g.*, Smee and Stanley, 2005). Analyses are generally on complete samples; size fractionation in the cuttings is likely to be an artefact of the drilling procedure. Analytical samples are generally collected by: -

- Grab sampling from individual spoil heaps;
- Splitting the cuttings as they leave the cyclone;
- Pipe- or spear-sampling cuttings in plastic or calico bags (Barnes, 1987). The bag is laid on its side and a PVC pipe, 50 - 60 mm in diameter is inserted diagonally through the cuttings; one or more samples are taken from each bag and combined.

Ideally samples should be collected throughout the profile, to take advantage of the dispersion haloes of the target and pathfinder elements in different horizons of the regolith. For reasons of economy, such full sampling is not normally practised except on a few orientation holes. As a compromise, samples may be collected from one or more ‘recognizable horizons’, from several set depths, of specific features such as redox fronts, or where the strongest ‘colour’ occurs (red, yellow or brown) to target Fe oxides, or at ‘bottom-of hole’, especially if this is close to fresh rock. Alternatively, aliquots of several samples may be composited for analysis and the individual sub-samples only analysed separately if anomalous concentrations are found.

Accurate logging of drill material is essential for correct selection of analytical samples and for data interpretation. This important, generally complex, aspect of saprolite sampling is often neglected or done poorly or inconsistently. Too commonly, logging is done in a very cursory manner during the supervision of a drilling program, and not subsequently checked or repeated. It is not, however, an easy task, and it can be very difficult to subdivide saprolite, in particular, into useful or consistently recognizable units, especially where it is powdered by drilling or features are obscured by strong colour variations. Commonly, the best that can be achieved is to establish boundaries such as "top of fresh rock" (weathering front), "base of complete oxidation", "base of alluvium" (unconformity between transported and residual units). Some consistency can be achieved by displaying small samples of drill cuttings from representative drill profiles in 'chip trays' or other containers. Comparison of an array of chip trays representing a drill traverse can assist in the recognition of larger-scale features. If the chips are wet sieved from a grab sample of drill cuttings, there is a danger that they may not be representative of the whole interval, especially from middle and upper parts of the saprolite. The resistant fragments may be from a specific small feature, such as a quartz vein or minor Fe oxide mottling, whereas the bulk of the sample is clay and has not been retained. However, wet sieving is a useful procedure; indurated or less weathered remnants form coherent, coarser materials that preserve fabrics useful for lithological logging.

Identification of bedrock lithology from drill cuttings can be difficult, but is assisted by maintaining a library of representative, properly characterized, samples, and by consulting appropriate reference documents (*e.g.*, Robertson and Butt, 1993). Instrumental techniques for the rapid logging of weathered and fresh rocks are being developed and should increase the information available from drill cuttings and core.

Saprolite samples should be analysed for a range of ore and pathfinder elements, including those that might represent the wider exploration target presented by primary alteration haloes (*e.g.*, potassic alteration associated with orogenic Au mineralization) and even lithological indicators. This is especially important where drilling intervals are wide and for deep samples close to bedrock. Total analysis is preferred. Chemical analysis can usefully be supplemented by rapid mineralogical analysis using visible to infra-red spectral techniques (*e.g.*, PIMA, ASD), targeting alteration haloes represented by specific mineralogical or lithological associations (*e.g.*, potassic alteration indicated by muscovite, which is readily detected by these techniques).

SOIL

DEFINITION

Soils are unconsolidated, surficial weathering products developed *in situ* from an underlying parent material under prevailing weathering conditions. In deeply weathered regions, the parent substratum is commonly weathered bedrock or some form of transported overburden. *N.B., the term 'residual soil' can be used to denote, and emphasize, that the soil has developed from a residual parent material. Conversely, the term 'transported soil' should only be used to refer to soil that has itself been moved, for example by landslip; soils on transported overburden have formed in their present location and hence are* in situ, *not transported.*

A mature soil in equilibrium with the local environment is typically differentiated into a number of *horizons*. These are soil layers approximately parallel to the land surface and differing from adjacent, genetically related, layers in physical, chemical and/or biological properties, or in characteristics such as colour, pH, structure, fabric, texture, consistency, and types and number of organisms. Soils may vary in character from thin, coarse-grained lithosols, that have only one or two poorly differentiated horizons, in some deserts, to thick, organic-, silt- and/or clay-rich soils differentiated into several horizons, in more humid regions.

Common soil horizons (Figure 6) include: -

- Litter (or O1): Plant (or animal) matter on the ground surface.
- O (or O2): Fibrous (peaty) or massive organic matter.
- A: Near-surface mineral horizon containing humified organic matter.
- E (or A2): Pale, commonly sandy, eluvial horizon with little organic matter, sesquioxides and clays leached or translocated to lower horizons.
- B: Illuvial horizons enriched in clay, and/or sesquioxides and/or organic matter derived from overlying horizons.
- C: Mineral horizon from which the overlying horizons are presumed to have been derived but that has been little affected by pedogenic processes. Remnant geological structures or fabric may be retained.
- D: Layers below the C horizon unaffected by the pedogenic processes that formed overlying horizons, *e.g.*, previously formed saprolite or transported overburden.
- R: Continuous fresh rock.

The A, E and B horizons are referred to as the solum.

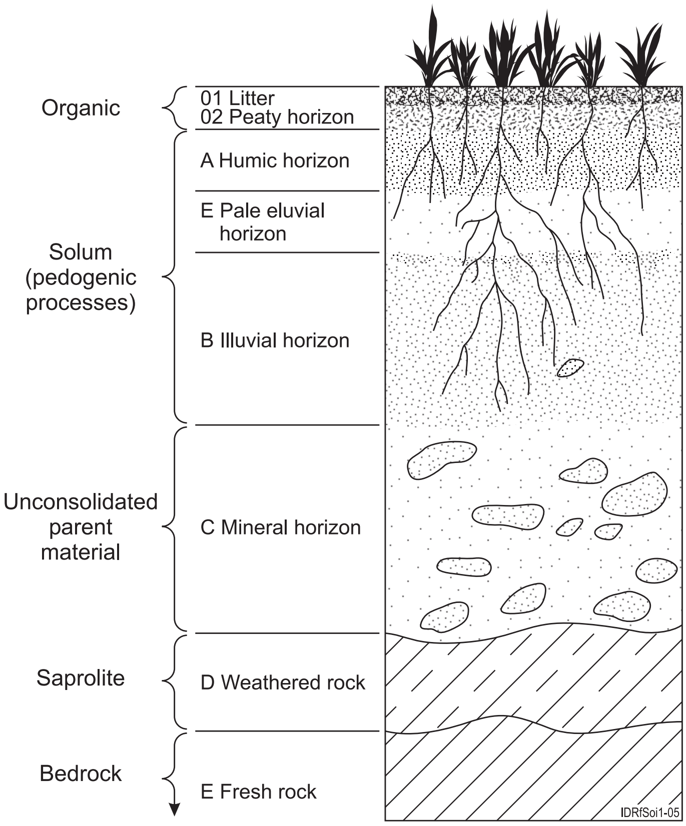

Figure 6. An idealized soil profile.

This terminology is ideally suited to well-differentiated soils such as podzols, but less readily applied to arid zone soils with weak horizon differentiation. In soils in semi-arid Australia, the B horizon may be differentiated from the A horizon by a contrast in texture and/or being more sodic or alkaline, rather than the characteristics noted above. The ferruginous zone of the lateritic profile should not be referred to as the B horizon.

FORMATION AND DISTRIBUTION

Soils are almost ubiquitous across the landscape, being absent only on rock outcrops, including inselbergs, actively eroding slopes, some ferruginous, siliceous or calcareous duricrusts, and active depositional areas such as talus, sand dunes and playa surfaces. Soils are formed by the interaction of climate, organisms (including vegetation) and vadose groundwater with the parent substratum over varying periods. Thus, there is a great variety of soil types in Australia, which have been subject to considerable study, particularly in agricultural regions; this work is summarized by CSIRO (1983).

Mapping and classification of soils has been based on two systems developed specifically for Australia. These differ from the two most commonly used international systems.

1. Great Soil Groups. The first soil map of the whole continent defined some ten major soil groups (Prescott, 1931), following a then prevailing international system. Soil genesis was discussed mainly in terms of the roles of climate and vegetation, although shortcomings, due to the influence of ancient weathering episodes, were recognized at the time. This system was modified by, and ordered on, the degree of differentiation of the soil profile (Stephens, 1962) and the degree of leaching (Stace *et al.,* 1968), to give seven Great Soil Groups and 43 sub-groups. The system is subjective and difficult to apply (Moore *et al.,* 1983).

2. Factual Key. A key for the unambiguous recognition of Australian soils was devised in part to facilitate compilation of the Atlas of Australian Soils completed in 1968 (Northcote *et al.*, 1960-1968; Northcote, 1979). It is based on attributes, measurable in the field, and the binary sub-divisions reduce ambiguity and misclassification. However, it mainly uses the A horizon and does not include any laboratory data, which lessens information about parent material and may combine materials of quite divergent origins and characteristics.

3. U.S. Soil Taxonomy. This is an entirely new hierarchical system, first published in 1975, and since revised (Soil Science Staff, 1999). It is based on field attributes and some laboratory-determined properties of diagnostic horizons, which subdivide soils into 12 orders. The terminology is logically constructed, but difficult for a non-specialist to comprehend. It allows a degree of international comparison. Because it is based mainly on examples from the USA, it has had less application in deeply weathered terrains.

4. World Soil Map. This was originally conceived as a global classification and has features that relate to the US Soil Taxonomy and to other, mainly European sources (FAO-UNESCO, 1988). It is simple, but thereby contains less information.

A comparison of these systems is given by Moore *et al.,* (1983). The soil maps should be relevant to mineral exploration but, in most cases, this is not so. They have been developed primarily for agriculture and, in their emphasis on surface horizons, largely ignore previous weathering episodes and parent material. Thus, in semi-arid parts of the Yilgarn Craton, most maps, including those based on soil taxonomy, do not indicate any affinities to deeply weathered terrain in other climatic zones. Generally, only those soils developed on residuum are of value as exploration sample media. However, the classification systems described above tend not to take properties of the soil parent materials into account, whether these are transported overburden, different horizons of a pre-existing regolith or contrasting bedrock lithologies.

Even though the Atlas of Australian Soils (Northcote *et al.,* 1960-1968) was based on landforms as the principal mapping tool, the units tend to cross important boundaries such as depositional to erosional, at least at the scale of compilation (1:2 000 000). The homogenizing effects of sheetwash and aeolian addition, especially in arid regions, further blur any local distinctions when classification depends largely on the uppermost horizons, as in the Factual Key. Nevertheless, regolith landform mapping can provide a sound basis for soil mapping for exploration, by providing a genetic context for the soil in terms of the weathering and erosional history, possibly with some broad lithological information. Thus, where pre-existing lateritic weathering profiles are well preserved (A models of dispersion: see Geochemical Models, *this volume)*, the soil has generally developed by the degradation of the upper horizons of the profile, *e.g.,* from lateritic residuum. It therefore consists predominantly of Fe and Al oxides and clay minerals, with some quartz. Where the pre-existing profile is truncated or never developed as a complete lateritic regolith (B models), residual soils have developed from saprolite, and consist dominantly of clay minerals such as kaolinite and smectite, with abundant quartz on granitic and sandy sedimentary rocks. Ferruginous fragments, and ferruginous staining of fine fractions, are common, especially over mafic and ultramafic rocks. Where the deep regolith profile has been completely stripped or has never formed (C models), residual soils have developed directly by weathering of fresh bedrock. The deeper horizons in particular may contain appreciable quantities of primary minerals, especially in areas of high relief and/or aridity.

In each case, the geochemical properties of the soil reflect those of the immediate parent material. A variety of different soils may develop within each regolith-landform regime, but their fundamental characteristic will be the same, modified by more local factors. Strongly differentiated soils, such as podzols, exhibit chemical and mineralogical partitioning. Components of stable minerals such as Ba (barite), Sn (cassiterite) and Au tend to remain throughout the soil profile, possibly with some relative accumulation in leached horizons. More mobile components, such as As, Cu, Pb, Zn, can be leached from upper horizons (O, A, E) to concentrate deeper in the profile, for example with Fe oxides in the B horizon. Some mobile elements may also be recycled through vegetation to enrich the organic-rich (O or A1) horizon. Strong differentiation is greatest in soils in humid areas, but can also be significant in arid regions, particularly with respect to carbonates and sulphates. A carbonate horizon may represent a pH barrier and cause the precipitation of mobile metals such as Cu (Mazzucchelli *et al.,* 1980), or concentrate Au, but in other situations carbonate is a diluent (Garnett *et al.*, 1982).

USE AS A SAMPLE MEDIUM

Soils are widely used (and abused) as geochemical sample media. The response largely reflects that in the parent material, but may be greater in area, due to additional mechanical and chemical dispersion during pedogenesis.

Lateritic regolith complete (A models). Geochemical responses in soils derived from lateritic residuum vary, depending on the element and on the relative proportion of the main mineral phases. As in the parent lateritic gravels and duricrust, mobile elements such as Zn and Ni are strongly leached, whereas others may be concentrated in Fe oxides. Sample preparation is thus particularly important, permitting the selection and concentration of specific mineral phases; the fine fraction may be mostly composed of quartz and clay minerals whereas the coarse fraction contains most of the Fe and/or Al oxides. Consequently, it is commonly preferable to collect the lateritic material itself or its lag; where this is not possible, the soil coarse fraction may give a similar response.

Lateritic regolith truncated or incompletely formed (B models). Geochemical responses tend to be very similar to those in the saprolite; abundances and contrasts may be lower due to leaching in humid areas or dilution by silicification and aeolian input or (except for gold), by calcrete in arid climates, but anomalies are greater in area. Accordingly, residual and semi-residual soils may be preferred to shallow saprolite as sample media on the basis of the geochemical response and lower cost of sampling.

Lateritic regolith absent (C models). The geochemical response of mineralization is very direct, yielding areally restricted anomalies of high contrast. Broader anomalies may occur in humid regions of moderate to high relief due to hydromorphic dispersion.

Because of the greater areal extent of soil anomalies, soil surveys are conducted prior to the more specific and costly saprolite and bedrock sampling. In relict terrain, it may be better to sample lateritic residuum (*see below*), rather than the coarse fraction of the soil; similarly, lag sampling (*see below*) may be preferred in some erosional areas. Soil surveys are particularly applicable to semi-regional to prospect scale exploration of areas of poor outcrop in which the soil is residual or semi-residual. Therefore, either before or during a survey, it is important to distinguish those soils that are likely to reflect bedrock composition from those that have developed partly or wholly from transported overburden and which, with rare exceptions, will show no geochemical relationship with the underlying bedrock. Nevertheless, not all anomalies in residual soils reflect mineralization. Some may be due to secondary concentrations in ironstones or weathered bedrock that form the parent material; such possibilities must be considered in data interpretation. Soil sampling grids should be run across strike, using spacings appropriate to the expected target size. Provided that a consistent sample medium is used, the data can be contoured or presented as stacked profiles to highlight zones of interest.

Despite the increasing availability of high quality multi-element analysis, the majority of soil surveys still rely on the determination of only the target element(s). There is, however, considerable merit in analysing for a wider range of elements, whether to explore for unexpected commodities or to assist in data interpretation. Multi-element analysis is of great value in determining the significance of base metal anomalies in areas where secondary concentration is a possibility or where hydromorphic dispersion is or has been active. The distributions of less mobile pathfinder elements (*e.g.,* Sn, W, Pb, Pt) can indicate whether such anomalies are related to a mineralized source and, if so, whether they have been displaced downslope during weathering. For example, at the Mt. Lindsay Sn prospect, Tasmania, As and Cu gave broader soil anomalies (B horizon) than Sn and W due to active hydromorphic dispersion (Ross and Schellekens, 1980). At Lady Loretta, Queensland, shallow (100 mm) soil sampling reflects past widespread leaching and dispersion of Zn, compared to the relative immobility of Pb and Ag, which have been retained in gossans and little dispersed (Cox and Curtis, 1977).

Multi-element surveys tend to emphasize target and pathfinder elements; major element soil geochemistry is comparatively little used but can be useful for: -

- Defining lithological changes in soil-covered terrains;
- Recognizing geological marker horizons in monotonous sequences;
- Mapping alteration haloes associated with mineralization;
- Normalizing data when minor element abundances are partly controlled by the presence of specific minerals, *e.g.,* Fe oxides, Ca and Mg carbonates;
- Determining the degree of surface leaching or evolution towards lateritization, *e.g.,* by ratioing Si or Fe contents with those of the alkali or alkaline-earth elements.

SAMPLING PROCEDURES

Soils are generally sampled from shallow pits dug by mattock or spade, by hand auger or power auger, depending on the depth of soil and the horizon sought. Except where a clean, deep pit is dug, some smearing or cross-contamination between horizons is inevitable. In poorly differentiated soils, *e.g.*, in some arid regions, it may be appropriate to simply sample below 100-150 mm, avoiding much of the transported component at the surface but, elsewhere, a more targeted approach is necessary – *e.g.*, to collect (or avoid) calcrete horizons or podzolic B horizons. Litter and organic A horizon sampling is effective where vegetative cycling of metals is suspected, especially if the soil is developed in transported overburden. Sampling of the A horizon can also provide a readily obtained, consistent sample type for regional sampling (Farrell and Orr, 1980). More generally, however, B horizon sampling is preferred, since it is commonly a zone of metal accumulation. The C horizon gives the most consistent samples, least affected by recent pedogenetic processes.

Depending on the results from orientation or previous experience, either the whole sample may be split and crushed for analysis, or a particular size fraction chosen. Within any particular soil horizon, other than those developed from lateritic duricrust and gravels, most elements tend to be fairly uniformly dispersed regardless of size fraction. This can be more apparent than real, because dry sieving is commonly ineffective in separating fine fractions. Clay particles aggregate and can coat coarser particles so that clean separations are rarely possible and analytical results are accordingly modified. Nevertheless, fine soil fractions are commonly convenient because metal contents are enhanced by the removal of barren quartz, and no further sample preparation is necessary prior to analysis.

Where there is substantial input of transported components, the soil response may be reduced by dilution. This may affect the whole soil or be biased towards particular –usually finer – fractions. Dilution by barren colluvium restricted the response of Cu-Au mineralization at White Dam, Curnamona Province (*this volume*), and at Beasley Creek, WA (*this volume*), a better contrast was obtained in the 710-4000 µm fraction than the whole soil, because of the high content of barren aeolian dust in the minus 710 µm fraction. Similarly, at Blayney, NSW, Dickson and Scott (1998) noted that the widely used minus 63 µm (80 mesh) fraction contained up to 80% aeolian material, which significantly diluted the geochemical signature.

Where soils are strongly differentiated, care must be taken to sample a consistent soil horizon. The use of a constant sample depth is not recommended, for profile conditions can change markedly along a slope. Where such consistency is not possible, the sample types collected must be documented for use in subsequent interpretation. The need to determine optimum sampling horizons and size fractions by orientation surveys cannot be overemphasized, nor can the need for adequate training and supervision of field samplers. *(NB. Cuttings from a 0-1 m composite of an existing deep auger, RAB or RC hole as a surrogate for shallow soil augering during an orientation survey may give misleading results due to cross-hole contamination. The intended sampling procedure itself should be used.)*

CALCRETE AND PEDOGENIC CARBONATE

DEFINITION

Calcrete is a generally indurated material formed by the *in situ* cementation or replacement, or both, of pre-existing regolith by authigenic calcite and/or dolomite (and, rarely, aragonite) precipitated from soil water or groundwater. Silica, magnesian smectites, barite and gypsum may also be present or even abundant. Carbonate contents vary considerably, and there is a wide range in morphologies and abundance from thin encrustations - for example, on freshly weathered (commonly mafic) rocks - to minor, diffuse enrichments, friable powders, pisoliths, nodules and concretions (to 100 mm or more) in soils, coarse nodular or slabby horizons and massive limestone rock. Although the term calcrete is conventionally applied to materials having >40% $CaCO_3$ (see Chen *et al.,* 2002a), lower concentrations can be geochemically significant, especially for Au exploration. Calcite is commonly the principal carbonate but, generally, dolomite also occurs. Where dolomite dominates, the material may be termed dolocrete (Goudie, 1983). Netterburg (1980) suggested a classification based on the calcite/dolomite ratio, but this is difficult to determine and probably of little practical value.

There are two principal genetic types, (1) pedogenic or vadose calcrete and (2) groundwater or phreatic calcrete, with numerous varieties between these end members. Pedogenic calcretes have considerable significance in exploration in southern, semi-arid regions of Australia, due to their ability to concentrate Au preferentially (Lintern *et al.,* 1992; Lintern, 2002; *see below*); conversely, they may also act as a diluent to base metals (Garnett *et al.,* 1982). Groundwater carbonates and associated sediments host U mineralization, dominantly as carnotite ($K_2(UO_2)_2$ $V2O_8{\cdot}3H_2O$).

Although the distinction between pedogenic and groundwater calcretes is not always clear-cut, this broad subdivision is useful to understanding their contrasting properties and significance to mineral exploration.

A detailed discussion of the characteristics and distribution of calcretes in Australia, and their use in mineral exploration, is given in Chen *et al.,* 2002a.

FORMATION AND DISTRIBUTION

Climatic control

Significant calcrete development on rocks other than limestones and dolomites typifies arid climates having 100-600 mm annual rainfall; their occurrence outside this range is interpreted as evidence for climatic change (Goudie, 1973; Mabbutt, 1977). In more humid environments, calcretes form only over limestone.

Pedogenic or vadose calcrete

Carbonates are precipitated in the unsaturated zone of soil profiles, commonly within 1-2 m of the ground surface, but deeper in some locations. Calcareous soils, with nodular calcretes in places, are associated with Au in the Kalgoorlie region as at Bounty (*this volume*) and Panglo (*this volume*). Massive calcretes (>1 m thick) occur on the Gawler Craton, as at Challenger (*this volume*) and Birthday (*this volume*) and occur extensively across southern Australia. These are calcrete landscapes II, III and IV (see Figure 7); they are characterized by winter rainfall and their northern boundary is at about 30ºS. In the Yilgarn Craton, this boundary is referred to as the "Menzies Line", which is, in fact, a narrow gradational zone having quite different vegetation, soil and groundwater on either side (Butt *et al.,* 1977). Some pedogenic carbonates occur farther north, *e.g.*, in dune sands in central Australia (landscape VI, Figure 7) but no Au-calcrete association has yet been recorded.

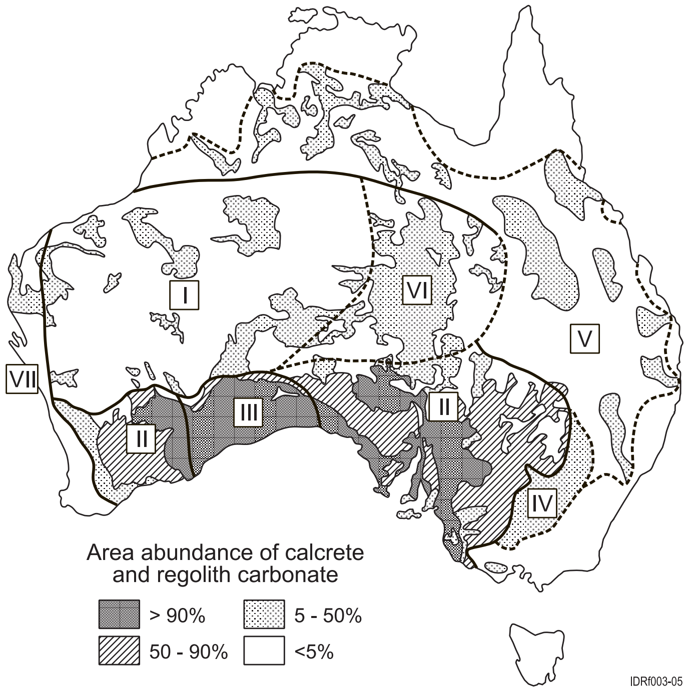

Figure 7. Interpretative distribution map of Australian calcretes, showing different calcrete landscapes (simplified after Chen et al., 2002b). I: groundwater calcretes in drainage axes. II: calcareous soils and nodular calcretes. III: boulder and laminar calcretes. IV: nodular calcretes in aeolian dust deposits. V: nodular carbonates in clay soils on Ca-rich parent materials. VI: nodular carbonates in aeolian sands. VII: crustal calcrete on limestones on the coastal plain.

Carbonate precipitation is caused by loss of water, by evapotranspiration and/or degassing of CO_2 in response to lower CO_2 partial pressures (in turn due to the decline of respiration at the end of the growing season or percolation of water below the root zone):

$$Ca^{2+} + 2HCO_3^- <==> CO_2 + H_2O + CaCO_3$$

Where pre-existing weathering profiles have been partly or completely stripped, the Ca is largely derived from the weathering of primary minerals; in such areas, there can be a marked lithodependence, with calcrete development strongest on mafic rocks. However, calcrete may also develop in highly leached, fully preserved, lateritic profiles, even in upland sites. Here, the derivation of the Ca is less clear, but it is probably from: -

- Aeolian accession of $CaCO_3$ deflated from coastal deposits or calcareous soils and sediments lower in the landscape.
- Accession, with other ions, as aerosols with rainwater.
- Capillary rise and surface concentration under an evaporation gradient.
- Uptake by plants from deep in the profile and surface precipitation after their decay.

Groundwater or phreatic calcrete

Carbonates are precipitated in the saturated zone, at or below the water-table, in colluvial and alluvial sediments that infill broad valley systems (Butt *et al.,* 1977). They typically occur as massive calcretes varying in width from a few hundred metres to several km, and to over 100 km in length, with longitudinal gradients generally less than 1:1000. Thickness is commonly 5-10 m but may exceed 30 m along the valley axis. They are major aquifers and, where they debouch into playas, they broaden out to deltaic platforms. Groundwater calcretes commonly form positive features in valley axes, forming mounds three metres or more above flanking alluvial plains. Upward growth is due to active carbonate precipitation at depth. The calcrete may show weak layering and a variety of heave structures, including pseudo-anticlines and diapirs, and karst and collapse structures near the surface. Authigenic silica and Mg-smectites, including sepiolite, are abundant locally.

Groundwater calcretes occur in central Western Australia, extending to the Northern Territory and South Australia (calcrete landscape I, Figure 7). In the W, the calcretes have been exposed by erosion following drainage rejuvenation and now cap terraces and mesas, but are still forming inland, in regions of largely internal drainage. These calcretes form in areas of mainly summer rainfall, where run-off, rapid infiltration and high evaporation and evapotranspiration limit the period of soil dampness and plant respiration. Dissolved Ca, Mg and bicarbonate remain in solution and enter the groundwater, only precipitating in drainage axes and depressions after concentration by evaporation or CO_2 degassing due to groundwater upwelling or capillary rise.

USE AS A SAMPLE MEDIUM

Exploration for carnotite uranium deposits associated with groundwater calcretes is not considered further in this volume due to the absence of any significant developments in the past 20 years. Their origin and numerous case histories are described by Mann and Deutscher (1978), Butt et al. (1977), Deutscher *et al.,* 1980a and Butt (1988).

The presence of pedogenic calcrete has both disadvantages and advantages for mineral exploration. The principal disadvantages are:

1. Many pedogenic calcretes represent absolute additions to soils developed on pre-existing deep weathering profiles which, in many instances, may have been partly truncated prior to soil and calcrete formation. The concentrations of most mobile elements (except, perhaps, Fe) associated with economic mineralization are already reduced by leaching during the initial deep weathering and later pedogenesis, so that calcrete precipitation causes dilution and depresses anomaly contrasts still further (Garnett *et al.,* 1982; Vermaak, 1984). The effects of dilution were demonstrated in South Africa by Garnett *et al.,* (1982), who found that abundances and anomaly contrasts at the Putsberg Cu deposit could be increased by removal of the carbonate by ammonium acetate leach and analysing the residue. Similarly, strong dilution of Ni and Cu in the calcrete horizon, compared to underlying saprolite, was noted at Pioneer, near Kambalda, WA (Cox, 1975). However, in both, the calcrete was developed in residual or semi-residual material and did retain a response, and hence was considered a more reliable sample medium than overlying soil, which has a much higher proportion of transported components.

2. The high pH commonly prevailing in the regolith of calcrete terrains reduces the chemical mobility of many elements and hence restricts the development of epigenetic hydromorphic anomalies.

3. Conversely, in some environments, the calcrete represents a pH contrast to underlying neutral to acid regolith and may cause the precipitation and concentration of leached metals, hence forming epigenetic anomalies at the base of the calcrete horizon. On the Yorke peninsular, SA, there is a significant Cu response at the calcrete-

clay interface to partial extraction (acid ammonium acetate) analyses (Kadina: Mazzucchelli *et al.,* 1980) and total analyses (Poona, *this volume*).

4. Gold can be enriched in the calcareous horizons of soils and may give rise to or enhance a near-surface expression to concealed primary or secondary mineralization. This property has led to pedogenic carbonates and calcretes being specifically targeted as a preferred sample medium for Au in southern Australia. Many discoveries have been made in areas having residual soil or shallow transported overburden, including Challenger (*this volume*), the first significant deposit in a new province, the Gawler Craton. Numerous case histories are summarized by Lintern (2002). These illustrate that carbonate sampling is effective even where developed in transported overburden, if this is no greater than 5-10 m thick. Although the limited dispersion suggests that calcrete sampling is most suited to local exploration and target definition, it has been used for regional surveys in the Gawler Craton with sample intervals as great as 1.6 km. However, concentrations are very low, with anomaly thresholds of 3 ppb Au or less.

SAMPLING PROCEDURES

Base metals

For exploration for base metals or other commodities where carbonate is anticipated to restrict dispersion and or act as a diluent, the following procedures are appropriate.

In relict terrain, with preserved lateritic profiles (A models)

- Preferentially sample lateritic residuum, analysing for a range of target and pathfinder element.

In erosional terrain (B models)

- Preferentially sample ferruginous lag, or ferruginous coarse soil fractions.
- Sample calcrete-free surficial horizons to obtain low contrast anomalies having some lateral dispersion but possibly diluted by clastic particles.
- Sample deep horizons below the calcrete to obtain higher contrast anomalies with minimal lateral dispersion.
- Use the calcrete horizon as a constant sample medium and search the data for restricted, low contrast anomalies. The dilution effect may be reduced by using a carbonate-poor fraction, by normalizing the data or by dissolving the carbonate and analysing the residue.
- Close sample intervals will be necessary, due to the restricted dispersion.
- In terrain where the carbonate horizon may form a pH barrier and potentially cause the precipitation of chemically dispersed metals, the carbonates and the underlying material, whether residual or transported, should be sampled by drilling. Ideally, all samples should be analysed; but, failing that, those across the lower contact should be selected for analysis, preferably by total and partial extraction methods.

Gold

In relict terrain, with preserved lateritic profiles (A models)

- Preferentially sample lateritic residuum, analysing for a range of target and pathfinder element. Nevertheless, associated carbonates may have similar or higher Au concentrations (Glasson et al., 1988).

In erosional terrain (B models)

- The carbonate horizon is preferentially targeted for Au exploration, because adjacent non-calcareous horizons will be essentially devoid of gold. Sampling procedures vary according to the type and depth of carbonate, and the presence of other material (Lintern, 2002). Indurated laminar calcretes, whether outcropping or buried, can be sampled in small pits and breaking with a crow-bar or hammer, or by drilling using a robust auger. Fine material, such as clay and sand, can be removed by sieving. Where silcrete is present, the calcrete horizon immediately above is commonly the site of highest Au abundance. Calcareous soils and powdery calcretes are best sampled by power auger, collecting the whole carbonate horizon (commonly in the top 1.5 m), excluding any non-calcareous topsoil. Accurate identification of the calcrete is essential at the time of sampling; testing for effervescence with dilute HCl is generally adequate, although more dolomitic samples can be slow to react. Because Au is distributed throughout the carbonate, a large sample is not essential, although conventionally a 30 g aliquot of a 1 kg sample is analysed. Samples should be crushed and analysed for Ca, Fe, Au and pathfinders such as As, Sb and W. An acid digestion (*e.g.,* aqua regia) is generally adequate, if there is sufficient acid to dissolve the carbonate fully; cyanide digestion gives good results, but for Au only. A detection limit of 0.1 ppb is recommended where abundance is low. The Ca data are useful to confirm that the sample is appropriate – lithic fragments with carbonate coatings, for example, may be mistaken for carbonate nodules - although gypsum may give misleadingly high Ca abundances. However, normalization of the data to the Ca content has not been shown to be effective. The Fe analyses will assist in interpretation of data for elements such as As, known to be scavenged by Fe oxides.

In depositional terrain (A and B models)

- If the total depth of transported overburden is less than 10 m, it is possible that preferential concentration of Au may give a surface expression to concealed mineralization. However, the contrast may be diminished. Caution should be exercised before interpreting a nil response as negative.

VEGETATION

DEFINITION

The use of vegetation in exploration programs involves either: -

- *Geobotany,* in which the distributions and/or morphological changes of specific indicator plants or plant associations are related to their preferential growth in soils having anomalous metal contents, nutrient status or other properties.
- *Biogeochemistry,* in which plant tissues or organs are chemically analyzed to detect biological concentrations of elements that may reflect mineralization.

These and associated topics are discussed in detail by Brooks *et al.,* 1995.

DISTRIBUTION AND ANOMALY FORMATION

Geobotany

Most of Australia is covered by vegetation (see Vegetation Communities, *this volume*), with climate, especially temperature and rainfall, being the principal controls on plant distributions and assemblages. Bedrock, regolith geology and land use mostly have a subsidiary influence at regional scales, but can be important at district to local scales. Consequently, the principle of mapping plant assemblages as a surrogate for underlying bedrock has long been applied in photogeology, and similarly contributes to the textural patterns used for regolith landform mapping by aerial photography and satellite imagery. Vegetation also contributes to the signal in hyperspectral surveys. Thus, in a general sense, geobotany is widely used as a geological tool. However, it has been little used directly for exploration in Australia, although it has been recognized that a number of plants indicate mineralization: -

- *Polycarpaea glabra, P. spirostylis and Tephrosia* spp. indicate Cu mineralization at Dugald River, Little Eva (*this volume*) and other sites in Queensland (Nicolls *et al.,* 1965; Brooks and Radford, 1978).
- *Gomphrena canescens, Polycarpaea* spp. and *Tephrosia* spp. were said to indicate carbonate hosted Pb-Zn mineralization at Bulman, NT, at its discovery in 1952 (Cole *et al.,* 1968).
- *Solanum linearifolium* grows preferentially near Pb-Zn

mineralization at Woodlawn, NSW (Wallin, 1976; Ryall and Nicholas, 1979).

- *Hybanthus floribundus* indicates Ni-rich soils on ultramafic bedrock in the Kalgoorlie region, WA (Severne, 1974).

These plants are all tolerant to metal-rich soils; *Hybanthus floribundus* is also a Ni hyper-accumulator. Each of the above species is part of broader associations in which either the plant assemblages may differ from those on surrounding soils with 'normal' metal contents, or specific species may be stunted, as illustrated by the detailed studies by Nicholls *et al.,* (1965) and Cole *et al.,* (1968). These effects are well developed in areas of outcrop and residual soil, but have little direct application where there is a thick, leached regolith or transported overburden.

However, the recognition and use of indicator plants need care, as the response may have only local significance or respond to stimuli other than high metal contents. In the Herberton area, Queensland, an apparent indicator plant for Cu-Pb-Zn-Sn mineralization at the Ivy Mine showed no such correlation only 3 km away (Groves *et al.,* 1972; Steveson and Taylor, 1973).

Biogeochemistry
Because of the cover of vegetation across nearly all climatic, geological and regolith-landform environments in Australia, there is a wide choice of plants for biogeochemical sampling. However, this choice is constrained by the need for the plants to have (i) appropriate root qualities, and (ii) a sufficiently extensive distribution at the scale of the survey. Plants have evolved to mitigate the stresses caused by the dry climates and nutrient-poor soils that prevail over much of Australia. One adaptation is the dimorphic root systems with shallow lateral and deep tap (or sinker) roots. The latter may reach 10 to >40 m and are able to access water and nutrients deep in the regolith, especially during dry periods and drought (Pate *et al.,* 1998; Aspandiar *et al.,* 2004). However, many plants are dormant at these times, so nutrient demand and transfer rates are potentially low. Some plants are phreatophytes, able to access water from the saturated zone or from the capillary fringe. The degree to which tap roots can tolerate highly saline groundwater is uncertain, and is a potential restriction on this mechanism of element transfer in much of semi-arid southern Australia and some environments elsewhere.

One of the principal tenets of biogeochemistry is that surveys should use the same plant organ from the same species, to reduce background variability. Despite the overall diversity (see Table 1 in Vegetation Communities, *this volume*), Australian vegetation is dominated by very few plant genera, namely *Eucalyptus* forests and woodlands (34%), *Acacia* forests and woodlands (19%) and hummock (spinifex: *Triodia*, *Plectrachne* spp.) and tussock (*e.g.*, Mitchell grass: *Astrebla* spp.) grasslands (32%). In addition, *Eucalyptus* and *Acacia* occur as subsidiary genera in many other vegetation groups, hence these trees and shrubs are the most commonly sampled plants for biogeochemical surveys. However, both genera have a very large species diversity, with considerable similarity and some hybridization between species, and it is unclear how important it is to maintain true consistency for surveys. Where they are absent, other deep-rooted trees and shrubs, such as cypress pine (*Callitris* spp.), bluebush (*Maireana* spp.), and poverty bush (*Eremophila* spp.) have been used.

Vegetation takes up a wide range of elements, from groundwater or mineral surfaces, utilizing some elements in the metabolic processes, but storing or rejecting others. Biologically essential elements (Ca, K, Mg, Na, S, Cu, Fe, Mo, Se, Zn,) are selectively taken up by vegetation. The elements may be disproportionately concentrated in plant tissue even where their abundances are very low in regolith and rocks (*e.g.*, high Cu contents in ashed *Eremophila* at Panglo: Lintern *et al.,* 1997). Non-essential elements, including those that are potentially toxic (*e.g.*, Ag, As, Au, Cr, Ni, Pb, Sb, U), are also taken up and may reflect more closely the composition of the substrate. These elements are subsequently released to the soil by decay after leaf-fall or the death of the plant, contributing initially to the litter horizon and ultimately to underlying soil horizons. Products derived from vegetation, such as litter and mull (decaying plant material) may have element concentrations greater than the original plant material due to (i) nutrient withdrawal during the senescence period immediately prior to leaf fall or (ii) preferential leaching of more mobile constituents including Ca, Cl, Mg and Na. Such mechanisms may account for high concentrations of base metals, including Sn, in litter over the buried Jaguar VHMS deposit, WA (Anand and Cornelius, 2004).

Although most will be recycled, there is potential for metals to accumulate gradually in surface soil horizons over time. If the soil is developed on transported overburden, this metal could be derived from depth via tap-roots and give surface expression in soil to buried mineralization. Uptake by vegetation may transform the chemical nature of elements in the regolith by, for example, forming organo-metallic complexes that, on release to the soil after plant decay, may impart a different mobility compared to the same metal bound in a mineral. These transformations may, in turn, influence partial extraction analyses. Cohen *et al.,* (1998) found only a poor correlation between vegetation and partial extraction soil anomalies (cold HCl, enzyme leach) in the Cobar District, NSW. This implied that the contributed metals had been flushed from the upper soil horizons and concluded that cycling by plants is not sufficiently active to cause significant surface enrichment. This conclusion needs further testing. A selectively sampled and/or analyzed soil horizon would have advantages over vegetation in terms of increased availability, reduced variability and cumulative response, *i.e.,* contributions by all parts of all plants over many generations, rather than by one organ of an individual plant at a specific time.

USE AS A SAMPLE MEDIUM

Biogeochemistry has been tested in a wide variety of environments and scales in Australia, with mixed success. There have been few regional surveys, with one of the largest being by Cohen *et al.,* (1999). Cohen compared vegetation and stream sediment surveys over a large area of NE NSW. Overall, vegetation was found to depend more on hydromorphic dispersion and to give broader dispersion trains from mineralization. Both media reflected regional variations, but there was little correlation on a site-by-site basis. Although known mineralization and new Au targets were indicated, these were generally in one sample medium only. At a district to prospect scale, there are a number of examples where metal contents of various plant species and plant organs have been shown to reflect mineralization beneath shallow residual soils, for base metals (Nicolls *et al.,* 1965; Cole *et al.,* 1968) and for gold (at Bounty, *this volume*; Lintern *et al.,* 1997; Panglo, *this volume*; Arne *et al.,* 1999, 2001). However, where the residual regolith cover is deeper and more strongly leached, plants may give poor response (Panglo: Lintern *et al.,* 1997). In general, sampling of residual soils and other shallow regolith materials is preferred, because it is easier and gives more consistent results. The greatest potential for biogeochemistry lies in areas of transported overburden, where tap roots and, if the cover is shallow, some lateral roots, may access weathered bedrock and deep groundwaters. This potential has yet to be tested fully, but there have been promising results at some sites, particularly for base metal mineralization: -

- Gold and base metal mineralization, Cobar NSW; shallow colluvium and skeletal residual soil. Multi-element anomalies in needles of white cypress pine (*Callitris columellaris*) (Cohen *et al.,* 1998; Mrangelli Pb-Zn-As prospect, *this volume*).

- Flying Doctor Ag-Pb-Zn prospect, Broken Hill, NSW (*this volume*); <5 m mainly coarse colluvium. Response in *Maireana* leaves, and *Acacia aneura* and *A. victoriae* phyllodes.

- Curnamona Province, SA: shallow calcareous soils on colluvium. Copper and patchy Au response in saltbush (*Atriplex vesicaria*), White Dam prospect (*this volume*).

- Jaguar VMS deposit, WA; 10-20 m alluvium and colluvium. Anomalous base metal and Sn contents in leaf litter and various organs of *Acacia aneura* over concealed, blind mineralization (Anand and Cornelius, 2004).

- Teilta, NSW; variable regolith cover in major drainage channels and alluvial outwash plains. Copper, Zn, As and Au anomalies in *Eucalyptus camaldulensis* leaves, with high seasonal variability (Hulme and Hill, 2004).

- Wyoming Au deposit, NSW; 20-40 m transported overburden. Anomalous Au and possibly As in *Eucalyptus microcarpa* and *Callitris columellaris* (Roach, 2004).
- Stuart Shelf, SA; 20-30 m sand and cover sequences. Copper-Fe-Zn anomalies in ashed Acacia twigs over porous non-calcareous cover rocks; no response through calcareous shales (Rattigan et al., 1977; Pernatty Lagoon, this volume).

Conversely, in the southern Yilgarn Craton, vegetation and mull sampling over several Au deposits gave equivocal results. Wherever there was an anomaly in these media, a similar or better response was found in the soil (pedogenic carbonate for Au), whether in erosional regimes (*e.g.*, Bounty; *this volume*) or areas of shallow (<10 m) transported overburden (Butt *et al.,* 1997a). At Zuleika, the response to concealed palaeochannel Au mineralization at 20 m depth gave a broad response in *Maireana* spp. on one section but only a smaller single point anomaly over higher grade mineralization on another; Eucalyptus gave no response (Lintern *et al.,* 1997). At Apollo, there were no anomalies in soil or *Eucalyptus* leaves above buried (60 m) mineralization, but *Maireana* again gave a strong response, although contamination is possible (Butt *et al.,* 1997a); the adjacent Argo deposit gave no response in soil, *Eucalyptus* leaves, *Eremophila* plants or mull. It is possible that the advent of analytical techniques with lower detection limits may yield responses but, at present, biogeochemistry appears to have little application for Au exploration in this region.

SAMPLING PROCEDURES

Trace metal contents in vegetation can vary according to the genus, species, organ selected (i.e., whole plant, leaves, twigs, bark, wood, roots, litter, mull), the age (*e.g.*, new growth, year old twigs) and season. Accordingly, the success of biogeochemical surveys depends on the selection of suitable samples for analysis and assiduous attention to maintaining these selections to achieve a consistent sample medium. This may present a challenge, because of the variable distribution within an area, similarities between species of the same genus and practical problems such a collecting leaves from tall trees. In general, it is desirable to composite at least three or four samples from each tree or shrub, collected using gloved hands and clean, preferably plastic-coated, instruments. Contamination by dust is a potential problem in arid environments and washing is commonly essential. The dried samples (70ºC) should then be cut, ground or milled and can be analyzed directly (*e.g.*, by neutron activation, or acid digestion and ICP-MS) or after ashing. The latter offers considerable concentration, but there is potential for loss by volatilization.

LATERITIC RESIDUUM

DEFINITION

Lateritic residuum is a collective term for the upper ferruginous zone of the lateritic profile (Figure 8), and consists of: -

- Lateritic gravel: an unconsolidated horizon of pisoliths and nodules (2-64 mm in size), and/or
- Lateritic duricrust: an indurated horizon that may retain primary structural or lithic fabrics, or have secondary fabrics, including pisoliths and nodules.

Where both horizons occur together, the lateritic gravel commonly overlies the lateritic duricrust. Lateritic residuum is composed dominantly of secondary oxides and oxy-hydroxides of Fe (goethite, hematite, maghemite), with minor Al hydroxides (*e.g.*, gibbsite, boehmite) and kaolinite, with or without quartz (Anand *et al.,* 2002). Exotic materials of colluvial or aeolian origin may be intermixed through lateritic residuum by soil-forming processes during and after lateritization.

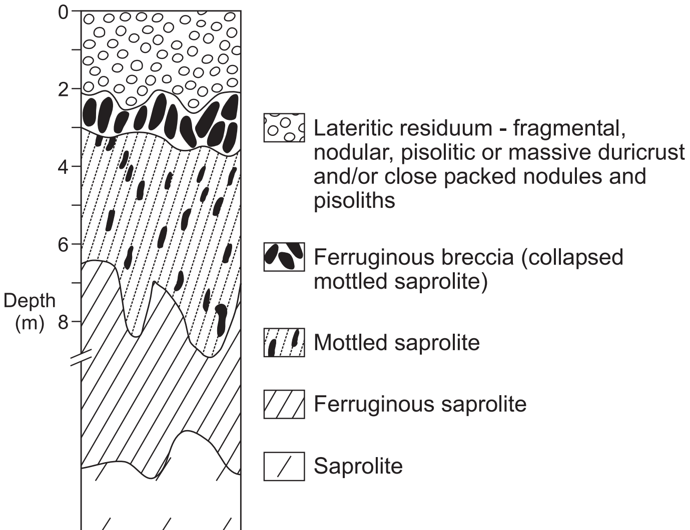

Figure 8. A typical weathered profile, including lateritic residuum at the top, passing down through ferruginous breccia of mottles, mottled and ferruginous saprolite and saprolite (after Anand et al., 2002).

The distinction between pisoliths and nodules is based on shape: pisoliths are spherical or ellipsoidal, whereas nodules are irregular. They may have one or more coatings or skins (cutans). An intact cutan on a pisolith or nodule implies that physical transport has been minimal. Pisoliths and nodules may be lithic or non-lithic. Lithic forms preserve rock fabrics and consist dominantly of hematite, goethite, kaolinite and gibbsite. Non-lithic forms have a clay- or sand-rich core, with one or more generations of Fe oxides (hematite, goethite and/or maghemite) disseminated through or replacing it. Both forms may retain resistant minerals in the cores.

Lateritic duricrust exhibits a variety of gross fabrics, including: -

- Lithic, essentially as intensely ferruginized saprolite and/or as a brecciated saprolite, showing the first stages of collapse. Primary structures, including shears and lithological contacts, are retained;
- Fragmental, with angular clasts;
- Massive, generally with small, partly filled voids;
- Vermiform, having numerous filled or partly filled tubes or pipes (possibly after roots) in duricrust with massive or lithic fabrics;
- Pisolitic or nodular, both clast-supported and matrix-supported. The cores of pisoliths and nodules may be lithic or non-lithic.

Similarly, lateritic gravels may have lithic and non-lithic components. Over Fe-poor rocks, such as sandstones and some granitoids, lateritic residuum may be poorly developed, represented only by mottles, nodules or pisoliths spaced within a sandy matrix, or absent.

FORMATION AND DISTRIBUTION

Lateritic residuum has evolved by chemical wasting, leading to partial collapse of mottled or ferruginous saprolite, or mottled clays, followed by Fe oxide precipitation, dehydration and pisolith and nodule formation (Anand *et al.,* 2002; possible x-ref to earlier chapter on weathering). These precipitation processes have probably been repeated many times. Collapse and consolidation have also involved lateral movement, commonly of the order of 5-50 m; hence the materials are better regarded as residual rather than *in situ*. The pisoliths, nodules and other ferruginous segregations that formed during this process are most important for mineral exploration because of their genetic relationship to the underlying bedrock. They may retain geochemical and mineralogical signatures of mineralization, alteration haloes and host rocks; hence they form valuable sample media. Low in the landscape, however, lateritic residuum may form in colluvial sediments deposited on weathering bedrock, resulting in a single regolith profile of mixed provenance. These sediments have little or no genetic relationship with underlying rocks; hence the lateritic materials developed from them are less suitable as sample media on a local scale.

The regional distribution of regoliths with well-developed lateritic residuum appears to be controlled by the primary lithology, past and present climate, and the erosional history. Lateritic residuum is most strongly developed on Fe-rich lithologies, such as ultramafic rocks, basalts, dolerites and some shales and occurs widely on these lithologies across the Yilgarn Craton of WA. It is thicker and more extensive in coastal areas where the climate is, or has been, more humid. On granitoids, thick Fe- and Al-rich lateritic duricrust and gravel are present only in the humid SW of Western Australia (*e.g.*, Darling Range). In the drier interior, E of longitude 117ºE, lateritic residuum on granitoids mainly occurs as gravel in a sandy matrix, with median contents of 19% Al_2O_3 and 20% Fe_2O_3 (Cornelius *et al.,* 2005a) compared to 16% Al_2O_3 and 40% Fe_2O_3. on dominantly greenstone rocks. On granitoids in the Darling Range, medians are 34.70% Al_2O_3 and 24.35% Fe_2O_3 Lateritic residuum is similarly widespread in warm humid regions such as the Pine Creek and Darwin districts, NT, but only developed on more ferruginous bedrock in the semi-arid Tanami Desert. In comparison, ferruginous materials are very sparse on the sedimentary basins of the interior of the continent, and over much of the Gawler Craton in South Australia.

In the Mt Isa region of Queensland (Weathering history, *this volume*), massive, fragmental and nodular duricrusts have formed residually on Fe-rich weathered rocks by accumulation of ferruginous materials from mottled saprolite after landscape down-wasting. Slabby duricrust has formed on lower slopes by induration of saprolite and locally derived colluvium by laterally accumulated Fe. It has a platy fabric and is rich in goethite, Mn and P.

Lateritic residuum is best preserved in poorly dissected regions, either exposed at surface or buried beneath later sediments. It characteristically outcrops in upper parts of the present landscape, on breakaways and upland plateaux that form relict regimes in the Yilgarn Craton, WA, or is shallowly buried on adjacent colluvial slopes. However, lateritic residuum can also be widely preserved in depositional regimes, buried by 30 m or more of colluvial-alluvial sediment (*e.g.*, Bronzewing, *this volume*). Remnants of presumably more extensive lateritic residuum occur in dissected regions such as the Mt. Isa and Charters Towers districts, Queensland (Weathering history, *this volume*).

USE AS A SAMPLE MEDIUM

The basis for the use of lateritic residuum as a sample medium (commonly loosely referred to as 'laterite sampling') is its close genetic relationship with underlying bedrock and its high content of Fe oxides. This relationship is demonstrated by the preservation of primary rock fabrics in duricrusts, nodules and lags (*e.g.*, Ora Banda sill; *this volume*). Where there has been lateral movement in the surface horizons during weathering, the value of the lateritic residuum as a sample medium may be increased, so long as the movement has been minor in the context of the whole landscape and the scale of exploration. Thus, cassiterite grains and gossan fragments in nodules, several hundred metres from the gossan outcrop at the Golden Grove VHMS (Smith and Perdrix, 1983; *this volume*) are reflected by a widespread geochemical anomaly.

Laterite geochemistry for mineral exploration in Western Australia was first used by Mazzucchelli and James (1966), who demonstrated a 180 m wide As dispersion halo around Au mineralization in the indurated ferruginous layer of a laterite profile, and in soils derived from it. It has since been shown to be appropriate for exploration from regional scales to target delineation for a wide range of commodity targets. In the SW Yilgarn Craton, Smith *et al.,* (1987, 1989) studied dispersion into pisolitic ferruginous duricrust in the Greenbushes rare metal pegmatite district and revealed a multi-element anomaly measuring approximately 20x12 km. Cassiterite and columbo-tantalite have been mechanically dispersed for at least 5 km. Based on the size of the anomaly, spacings of up to 3 km were suggested for pisolith samples in areas of high relief. Smith and Perdrix (1983) demonstrated a 1.5x2 km wide Bi-Sn-Mo-In-Sb-As-Cu-Au anomaly in pisolitic laterite at the Gossan Hill and Scuddles deposit, Golden Grove, WA, and a Au-As-Bi-Sb-W-Pb anomaly at the Mt. Gibson Au deposit, WA (Smith and Anand, 1992; *this volume*). These anomalies are detectable by 1 km spaced sampling. More detailed sampling, to as close as 50 m intervals, can be suitable for target definition, such as at the Callion Au deposit, WA, where pisoliths were an important component of soil samples (Glasson *et al.,* 1988). Similarly, Au-As anomalies in buried laterite at Mt. McLure and Bronzewing are sufficiently well constrained to define drill targets. Sampling strategies suited for different stages in exploration are summarized in Table 3. During the period 1980-1993, a regional laterite geochemical database (CSIRO-AGE) of several thousand laterite samples (Grunsky, 1991; Grunsky *et al.,* 1988; Grunsky *et al.,* 1989; Geological Survey of WA, 1998) was generated, covering substantial parts of the Yilgarn Craton, including greenstone-dominated areas with poor outcrop. This was supplemented by further sampling for diamond exploration during 1997-2001 (Cornelius *et al.,* 2005a, b). A laterite geochemical atlas of the western Yilgarn Craton, based on a 9 km triangular grid, is currently in progress (Cornelius and Morris, 20005), with the intention of covering the whole Craton. Massive, fragmental and nodular duricrusts in the Mt Isa area, Queensland have similar potential for district- to prospect-scale geochemical surveys.

TABLE 3
REGIONAL SAMPLING STRATEGIES

Sampling stage	Relict terrain	Erosional terrain	Depositional terrain (Laterite preserved)
Reconnaissance	Pisoliths or nodules at surface; 3-9 km spacing	Small pockets of pisoliths or nodules at surface; 3-9 km spacing	Pisoliths or nodules; 3-9 km spacing (drill/dig or locate erosional windows)
Regional	Pisoliths or nodules at surface; 3 km spacing	Small pockets of pisoliths or nodules at surface; 3 km spacing	Pisoliths or nodules; 3 km spacing (drill/dig or locate erosional windows)
Follow-up	Pisoliths, nodules or ferruginous duricrust; 1 km spacing	Lag of lateritic residuum at 100-300 m spacing, Fe-rich saprolite at 20-100 m spacing	Pisoliths, nodules or ferruginous duricrust; 1 km spacing (drill/dig)
Target delineation	Ferruginous duricrust; 50 m spacing	Ferruginous mottles and Fe-rich saprolite at 5-20 m spacing	

After Cornelius et al., 2001.

SAMPLING PROCEDURE

Lateritic gravel and duricrust have developed by partial collapse, which involves both vertical and lateral movement, during chemical wasting, as noted above. They may be regarded as essentially residual if this movement amounts to only a few tens of metres (or even 100 m or so, depending on the scale of exploration). It is this limited dispersion that makes laterite sampling a powerful exploration tool, subject to correct identification of its origin and provenance. Even where buried, lateritic residuum is an effective sample medium, but it is essential to distinguish it from distally transported lateritic debris. This significant transport is common in the sedimentary cover and may directly overlie either lateritic residuum (*e.g.*, at Bronzewing: *this volume*) or saprolite (*e.g.*, Golden Delicious: *this volume*; Quasar: *this volume*). Such debris is genetically unrelated to the underlying material and is inappropriate as a sample medium on a local scale. It can generally be identified by its polymictic nature, the lack of pale, goethite-rich cutans on pisoliths and nodules and angularity of fragments. Where deposited directly over saprolite, the abruptness of contacts, possibly with mineralogical changes (*e.g.*, absence of resistant minerals such as talc and muscovite present in saprolite) are additional criteria. However, pisoliths and nodules that have developed in the sediments themselves, after deposition, may have prominent cutans, a feature commonly observed in palaeochannels.

Sampling of lateritic gravel and duricrust should always be in a regolith-landform context to avoid inadvertent sampling of ferricrete or other 'non-lateritic' material. Plateau surfaces on lateritic residuum adjacent to small erosional scarps or 'breakaways' provide much geological information and good sample sites even in areas of thick sandplain. Suitable sample sites in sand-covered terrain are generally relatively small (5-10 m across) and difficult to find except from the air. Here, a regolith map, Landsat (TM) image or airborne radiometrics may assist identification of suitable sampling areas. Where shallow soil or sand covers lateritic residuum, it has to be excavated, which requires a good understanding of the landform setting to ensure success. Where the profile is stripped to saprolite, remnants of lateritic residuum may be preserved in shallow pockets 0.5-1 m in diameter. Locally derived (colluvial) ferruginous detritus, or lateritic lag, may be trapped in cracks and depressions. Where truncation is severe, however, even this may be lost, so that laterite sampling cannot be used.

Regional sampling should be without regolith or bedrock bias, unless there is an established connection with the targeted commodity. For example, preferential sampling of ferruginous material near quartz veins could bias the samples towards sub-economic vein-hosted mineralization because their geochemical signature could obscure a weak, regional, multi-element signature of a larger ore body of a different type. Similarly, lateritic gravel should be collected without bias towards specific types of pisolith or nodules. However, those with well-developed cutans are preferred, since they imply restricted transport. Physical characteristics (shape, colour, size) should be documented to assist with interpretation; Smith *et al.,* (2000) discuss preferred sample hierarchies for different terrains (exposed lateritic residuum, lateritic residuum buried beneath terrestrial sediments and beneath sedimentary basins). Laterite samples need to be representative and a minimum of 1 kg should be collected over a 10 m radius, if sufficient material is available. Where lateritic gravel is scarce, the search radius may have to be larger. Drill spoil from reconnaissance or past exploration drilling may also yield samples in extensive depositional areas. Because less mechanical dispersion has generally occurred during their formation, duricrusts are more suited to later stages of exploration and the definition of drill targets than lateritic gravel. Analysis by a variety of sensitive total analytical techniques is essential, to ensure detection of elements hosted by resistant minerals.

LAG

DEFINITION

Lag is the accumulation of coarse, usually hard, fragments of diverse origins or compositions that forms a veneer or pavement on the land surface. In an exploration context, lag commonly refers to highly ferruginous materials, including pisoliths, nodules, fragments of ferruginous saprolite, mottles and other segregations. In some circumstances, other materials such as calcrete fragments, could be targeted.

FORMATION AND DISTRIBUTION

Lag fragments generally range in size from granules to cobbles (2-256 mm), and are left following the physical and chemical breakdown of the upper regolith and removal of finer material in solution or by sheetwash, wind or churning. Ferruginous lag is composed dominantly of hematite, goethite and maghemite, which readily adsorb or incorporate a wide range of indicator elements (Carver *et al.,* 1987; Robertson, 1996), making it a suitable sample medium for Au, base metal, rare metal and Ni exploration. Lag is widely distributed in arid environments, across both residual and depositional terrain. In residual terrain, due to the dominantly erosive processes associated with the release and accumulation of lag at surface, local mechanical dispersion is expected. Nevertheless, lag components are genetically related to the underlying bedrock, a relationship that may be preserved even where residual soils have considerable dilution by aeolian and fine alluvial materials. In depositional areas, however, surficial lag may have no genetic relationship with underlying bedrock, since it has either been transported by sheetwash or released from sediments of distal provenance.

USE AS A SAMPLE MEDIUM

Regolith-landform control is very important when using lag as a sample medium. Lag is effective in relict and erosional regimes, i.e., areas characterized by widespread preservation of the lateritic mantle and those where bedrock, saprolite or mottled zone are exposed at surface or covered by thin soil or locally derived alluvium and colluvium. Surface lag is unlikely to show the geochemical signature of the residual regolith or bedrock in depositional regimes where there is a cover of exogenous sediments several metres thick. The use of buried lag, along the unconformity, may be used (see Interface sampling).

Geochemical anomalies in fine lag are generally broader than those in soil, due to enhanced mechanical dispersion at the surface (Robertson, 1996). Lag geochemistry also shows weak bedrock mineralization much better than soil, *e.g.*, for base metals and barite in the McArthur Basin, NT, and may show a better anomaly contrast than soil, *e.g.*, for Ni sulphides in the Eastern Goldfields WA, (Carver *et al.,* 1987). Where the composition of lag varies strongly, for example, due to dilution by coarse quartz sand, Carver *et al.,* (1987) recommend normalizing trace element concentrations using regression analysis based on the Fe content, although for some elements (*e.g.*, Cu, Zn) changes in the type of Fe oxide mineral can result in lower abundances at higher Fe concentrations (McQueen *et al.,* 2004).

The interior fabric of lag can provide evidence of the underlying rocks and their weathering history. Lag derived from ferruginous saprolite is considered most useful although duricrust-derived lag may also retain lithic remnants (Robertson, 1995; Ora Banda Sill, *this volume*).

SAMPLING PROCEDURE

Lag is sampled by simply sweeping unconsolidated material from the surface and screening particles (Carver *et al.,* 1987). Both coarse (10-50 mm) and fine (0.5-10 mm) lag are effective sampling media, but the use of coarse lag in Au exploration requires large (>>1 kg) samples to minimize any potential nugget effect. Coarse lag tends to resist aeolian and sheetwash action better than fine lag and therefore may show less lateral dispersion, making it more suitable for follow-up (Robertson, 1996). Fine lag can be obtained even in areas of dune cover, such as the Paterson Province within the Great Sandy Desert, WA, where termite mounds are abundant and termite activity has transported fine lag to the surface where it is redistributed (Carver *et al.,* 1987). An orientation survey will determine the best size fraction for a given commodity and specific area. Where lag is sparse, the relatively coarse, ferruginous fraction (0.5-10 mm) of the soil, sieved out on site, may provide a sample equivalent to fine lag.

Commonly, a proportion of lag (less than half) is may be magnetic, due to maghemite. This has been generated mainly by heating from bush fires (Anand and Gilkes, 1987). Maghemite lag can be separated using a handheld magnet and provides a very consistent sample. However, in general, it may not be an ideal sample medium. Not only are important adsorbed target and pathfinder elements lost with the recrystallization to maghemite, but non-magnetic components, such as gossan fragments, similarly enriched in these elements (*e.g.*, Cu, Pb and As), are specifically excluded as they are non-magnetic as noted at Bottle Creek (Robertson and Wills, 1993; Anand, 2001) and Beasley Creek (*this volume*, and Robertson, 1989). Gold was found in both the magnetic and non-magnetic components. As no significant advantage can be gained by separating and using the major non-magnetic component, analysis of the total lag is recommended. Nonetheless, it may only be practical to use magnetic lag if ferruginous components are sparse, such as where aeolian cover is widespread, but the response to mineralization may be comparatively subtle or muted in some elements.

FERRICRETE

DEFINITION

Ferricretes are indurated materials formed by the *in situ* cementation of transported regolith by Fe oxides, mainly goethite and/or hematite. The matrix may consist of a wide range of colluvial and alluvial sediments. Where these are transported lateritic gravels, the ferricrete may be difficult to differentiate from residual lateritic duricrust. A toposequence in lateritic terrain may show a continuum from lateritic residuum on the hillcrest through to a ferricrete in the valley floor

FORMATION AND DISTRIBUTION

Ferruginized sediment, or ferricretes, can form through (i) cementation of detrital clasts, sand or clays by Fe oxides or a mixture of Fe oxides and gibbsite or kaolinite; (ii) precipitation of authigenic hematite and goethite-rich pisoliths and nodules in sediments; (iii) precipitation of ferruginous masses in seeps and drainages, commonly in association with organic matter (*e.g.*, as bog iron). Thus, ferricrete outcrops may mark former lakes, swamps, discharge sites (seepages), valley floors, aquifers or zones of groundwater-mixing, including past water-tables and redox fronts. They may be buried or, following exposure and induration, form low hills due to relief inversion. Importantly, there is no genetic relationship between the ferricrete and the underlying weathered or fresh rock (Anand and Paine, 2002).

USE AS A SAMPLE MEDIUM

Ferricretes, including authigenic nodules and pisoliths formed in sediments, will commonly not show a geochemical signature that relates to the underlying or nearby bedrock, hence their use as a sampling media is restricted. However, some, *e.g.*, transported and recemented lateritic gravel, may have an application in widespread reconnaissance sampling in the absence of residual lateritic gravel. It is also possible that ferricretes in seeps and drainages, dominated by reprecipitated Fe (and Mn) oxides, might concentrate metals dispersed hydromorphically from concealed mineralization. However, their use in exploration would require a good understanding of regional regolith-landscape evolution, palaeotopography, and past and present drainage to determine probable directions of dispersion, and to account for false anomalies generated by the scavenging of metals leached from country rock.

SAMPLING PROCEDURE

Ferricrete should be sampled in the same manner as lateritic gravels and duricrusts. If ferricretes are included within regional laterite surveys, it is imperative to be able to separate them from lateritic residuum during data processing and interpretation. It is possible that the detrital, ferruginous gravel and the matrix might distinguish between distal and local geochemical signatures, respectively, hence ideally, these components should be analysed separately.

SILCRETE

DEFINITION

A feature of the semi-arid to arid interior of Australia is the extent of silica-indurated materials. In most of these, the silica is a relatively minor addition so that the precursor is readily identified and its properties are little changed. Red-brown hardpan, a widespread surficial unit in central WA and parts of NT and SA, for example, consists of a variety of transported or residual host materials including colluvium, nodular gravels and brecciated saprolite cemented by a porous matrix of silica (commonly hyalite), alumino-silicates and Fe oxides. Hardpan is generally not strongly cemented and fractures readily. In comparison, silcretes are strongly silicified, highly indurated and generally of low permeability; they commonly have a conchoidal fracture with a vitreous lustre. They appear to represent the complete or near-complete silicification of a precursor regolith by the infilling of available voids. The induration is such that fractures propagate across enclosed quartz grains, rather than around them. Silcretes may be classified broadly into pedogenic or groundwater types. Most are dense and massive, but some may be cellular, with boxwork fabrics. The fabric, mineralogy and composition of silcrete may reflect those of the parent (regolith) material and hence, if residual, the underlying lithology. Thus, most silcretes over granites and sandstones have a floating or terrazzo fabric, with residual quartz grains separated by a matrix of cryptocrystalline quartz, anatase and zircon, reflected by enrichment in Ti and Zr (Smale, 1973; Hutton *et al.,* 1978; Butt, 1985); silcretes with lithic fabrics (*e.g.*, on dunites) are silicified saprolites with initial constituents diluted or replaced by silica.

DISTRIBUTION

Silcrete is found mainly in the semi-arid to arid interior of continental Australia, mostly developed on sandstones and granitic rocks. Here, they form surface or near-surface horizons, commonly 1-2 m thick, in places forming the resistant upper unit on erosion scarps (breakaways). On the Gawler Craton, silcrete and other siliceous materials (hardpan, silicified saprolite, claycrete) are abundant in the upper 3-6 m and, in rare exposures (*e.g.*, the open pit at the Challenger mine), exhibit a complex history of cementation, brecciation and recementation (Lintern, 2004). At Mulga Rock (*this volume*), intense silicification of Tertiary (possibly Miocene) sandstones has formed columns and sheets of silcrete in the top 10 m, although outcrop is rare. Silcrete also forms on other lithologies, particularly dunites and limestones.

On dunite, massive silicification of saprolite generally occurs just above the Mg discontinuity, but extending deeper along veins and fractures (*e.g.*, Mt. Keith: *this volume*). The silica was derived from the weathering of serpentine and remnant olivine. Where erosion has taken place, such silicified saprolite outcrops as a resistant caprock. Commonly, this silcrete shows perfect preservation of the primary rock fabric. In places, however, the silica has precipitated along grain boundaries of Fe oxide pseudomorphs after olivine; when the oxides are lost, the resultant silcrete has a highly porous boxwork fabric. Weathering of limestone and dolomite releases silica, which precipitates as a brecciated silcrete, resistant to erosion. Cryptocrystalline quartz and opaline silica are also precipitated in calcretes. When these are weathered and eroded, the silcrete again forms a resistant unit, resulting in a locally inverted topography, in which the calcretes form mesas and terraces above the rejuvenated drainage (*e.g.*, in the Gascoyne Province, WA: Butt *et al.,* 1977).

USE AS A SAMPLE MEDIUM

Silcrete is rarely deliberately selected as a sample medium, although it may form a component of other media. Where the silcrete has formed by silica flooding of residual regolith materials, whether these are soils or saprolite, it will retain original mineral and geochemical characteristics of the precursor, including evidence for mineralization:

- Over granite and some sandstones, Zr and Ti have been concentrated prior to and possibly during silicification (Butt, 1985) to give a recognizable geochemical signature.
- Silcretes on dunitic rocks have Ni and Cr contents that indicate the parent lithologies, *e.g.*, where they outcrop as caprocks. However, this silicification results in dilution; in silicified saprolite at Mt. Keith (*this volume*), the Ni content is inversely proportional to the silica content of the silicified saprolite (Butt and Sheppy, 1975). This silicification is rarely complete on a bulk scale, hence the siliceous zones in oxide Ni laterite deposits, which overall have sub-economic Ni contents, can be upgraded by screening to remove the hard, coarse, low grade siliceous component, and retaining the finer, higher grade Fe oxide fraction.
- Silcretes associated with calcrete U deposits are enriched in U (to >100 ppm), may fluoresce and give a radiometric response in outcrop (Butt *et al.,* 1977).

At the Federal pit, at Broad Arrow, north of Kalgoorlie, there are Au anomalies (50 ppb in a background of 10 ppb) in red-brown hardpan cementing colluvium. These are thought to be due to both mechanical and hydromorphic dispersion (Mahizhnan, 2004; Mahizhnan et al., 2005) and could be used as a useful sampling medium for Au exploration.

Because of its widespread occurrence as a near-surface unit in the Gawler Craton, silcrete has been tested as a possible sample medium for Au exploration (Lintern and Sheard, 1998; Challenger, *this volume*). Samples of silcrete lag from the Challenger Au deposit show a prominent Au anomaly (maxima 50-105 ppb) over outcropping mineralization, but little or no response where there is a cover of transported overburden. This compares somewhat unfavourably with calcrete, which has a more consistent Au content, again at 50-100 ppb, but also has peak concentrations >2000 ppb over outcropping mineralization and shows a response to one zone of shallowly-buried mineralization. Whereas Au appears to concentrate specifically in calcrete and is evenly distributed, in silcrete, Au has a highly variable distribution, with some individual sub-samples having extreme Au concentrations. Silicification is probably retaining (and diluting) particulate Au in the precursor. The results suggest that silcrete has potential as a sample medium in the absence of calcrete, but will only be effective if developed in residual materials. Hill (2003) has suggested the use of silcrete as a regional exploration sample medium on the Curnamona Craton.

SAMPLING PROCEDURE

Silcrete lag can be collected from the surface, preferably compositing numerous small fragments over a 10 m^2 area. As with ferruginous lag (above), the use of coarse fragments (10-50 mm) requires large (>> 1 kg) samples to minimize any potential nugget effect. Outcropping and subcropping silcrete, including silicified saprolite, may be sampled from drill cuttings, again using large, well-mixed samples. Total analytical methods are necessary to ensure detection of Au particles encapsulated by silica.

INTERFACE

DEFINITION

'Interface' sampling refers to sampling across an unconformity, generally that between weathered basement and cover. In most exploration geochemical sampling, a single, specific medium should be taken to ensure data are comparable. Interface sampling is unusual, in that it deliberately uses a mixed medium, i.e., transported overburden above and weathered basement below.

FORMATION AND DISTRIBUTION

Interface sampling is based on the possibility of dispersion at or close to the unconformity by the following mechanisms (Figure 9): -

- Mechanical dispersion of remnants of lateritic duricrust or lateritic residuum down slope or as small fluvial concentrations of these materials.
- Mechanical dispersion from mineralization of mineral grains and gossan fragments in remnants of buried fossil lag or colluvial palaeosol, and hydromorphic dispersion associated with palaeosol formation.
- Hydromorphic dispersion after deposition of the cover by groundwaters percolating through the coarse, basal sediments, along the unconformity itself and/or the upper residual material. This dispersion mechanism may still be active.

One or more of these mechanisms may have operated in any location where transported overburden is present. They can give rise to lateral dispersion haloes at the base of cover in which there is no evidence of upward dispersion into soil.

Dispersion of gold and associated elements in basal colluvium at Mt Gibson (Anand *et al.,* 1989; *this volume*), Mt McClure (Anand *et al.,* 1993), Lawlers (Anand *et al.,* 1993) and Bronzewing (Varga *et al.,* 1997; *this volume*) indicated that sampling close to the unconformity could be a useful procedure, where the deepest transported units were composed of lateritic gravel. In significantly truncated regimes, where there is no such locally-derived lateritic gravel, sampling across the unconformity provided less intense but broader geochemical targets than sampling the top of the basement. This is demonstrated at Quasar, WA, beneath 4-6 m of colluvium-alluvium (Robertson *et al.,* 1994; *this volume*) and Harmony, WA, under 1-9 m of colluvium (Robertson *et al.,* 1996; *this volume*)

Dispersion is also evident along more deeply buried unconformities at Eloise, Queensland (*this volume*), where weak Au and Cu dispersion extends down slope from mineralization, beneath more than 100 m of barren fluvial and clay-rich Mesozoic sediments (Li Shu and Robertson, 1997). Lead is dispersed for several hundred metres at the unconformity at depths of 20-30 m at the Waterloo base metal deposit, Queensland (*this volume*). Stronger and more significant haloes are reported along unconformities both at the base of the sedimentary cover and along discontinuities and fractures within the sediments themselves. This is evident at Osborne (Lawrance, 1999; *this volume*) and Thalanga (Granier *et al.,* 1989), where dispersion is thought to have occurred in several episodes during burial and subsequent weathering. Although dispersion has been depicted as wholly within sediments at both Waterloo and Thalanga, it may be on the basal unconformity, due to an error in logging.

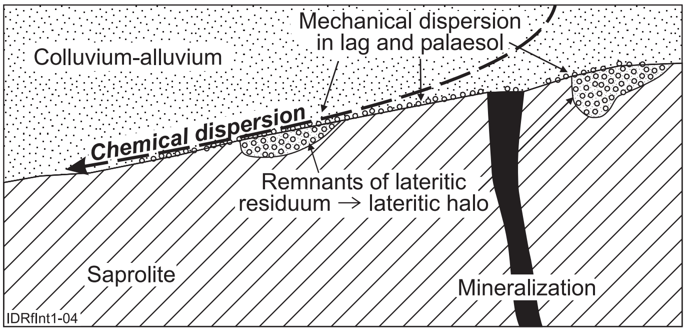

Figure 9. Dispersion model for a colluvium-covered erosional regime suitable for interface sampling. Dispersion in the top of the basement consists of weak, limited dispersion in saprolite and scarce remnant pockets of lateritic residuum. Dispersion along the unconformity consists of mechanical dispersion in a lag or palaeosol and chemical dispersion along or close to the contact.

USE AS A SAMPLE MEDIUM

Interface sampling is useful in areas of extensive transported overburden, especially where the buried residual profile has undergone significant truncation. Where the pre-existing profile has been little eroded and lateritic residuum is widely preserved beneath the cover, this should be targeted instead (Smith *et al.,* 2000). Both methods require drilling through the cover.

Interface sampling is most successful where the sedimentary environment was of low energy, dominated by soil creep, sheetwash or, at most, ill-defined, slow-flowing streams, depositing sediment as gently inclined fans. Such situations favour the preservation of detectable amounts of mechanically dispersed mineralized detritus, which may be supplemented by later, hydromorphic dispersion. In contrast, in high-energy, fluvial environments, such as at Pajingo (*this volume*), anomalous detrital material would be scoured away and diluted. Any geochemical response would then depend on post-depositional hydromorphic dispersion at the unconformity. However, in such active environments, localized dispersion trains may form higher in the sedimentary column, distant from the subcrop of the mineralization..

SAMPLING PROCEDURE

The base of the cover can be a simple, sharp, erosive unconformity (Figure 10A) or a complex mixture of saprolite and colluvium, a metre or more thick (Figure 10B), possibly including a palaeosol, which has later been buried (Robertson *et al.,* 1999). In a clay-rich environment, a mixed zone as much as 10-15 m thick may have formed by post-depositional churning (*e.g.*, Mt. Keith, *this volume*). Ideally, the position of the unconformity should be logged accurately. This is generally only possible from drill cuttings if there is a useful contrast (colour or texture), or the abrupt appearance of minerals or other components typical of either the sediments (*e.g.*, rounded grains, abraded pisoliths) or the bedrock (*e.g.*, mica). In the future, hyperspectral analysis of mineralogical characteristics such as kaolinite crystallinity may be used routinely to assist conventional logging.

In low energy depositional environments, if it is possible to locate the unconformity to the nearest metre, the metre interval crossing the unconformity that includes both basement and cover materials is an ideal choice (Figure 11A). If a mixed sample cannot be identified, the metre intervals above and below the unconformity can be collected (Figure 11B) and composited to ensure the unconformity is included.

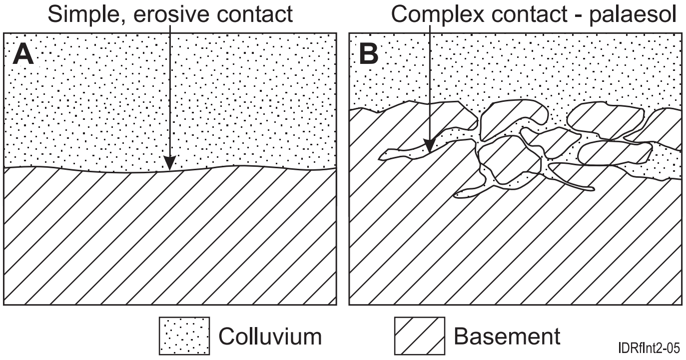

Figure 10. The base of the cover may form a simple erosive contact (A) or a more complex mixture of cover and basement as a palaeosol (B).

Where the contact cannot be clearly defined, collecting and analyzing several separate samples across the contact is preferred, since dispersion may be less well confined. Here, several individual samples are recommended rather than compositing more than two metre intervals across this interval, as this would dilute the response.

In higher energy depositional environments, with steeper depositional gradients, anomalous detritus may occur higher in the stratigraphic column and not necessarily at the base (e.g., Pajingo, *this volume*). This necessitates sampling throughout the cover and using either a mean or a maximum value.

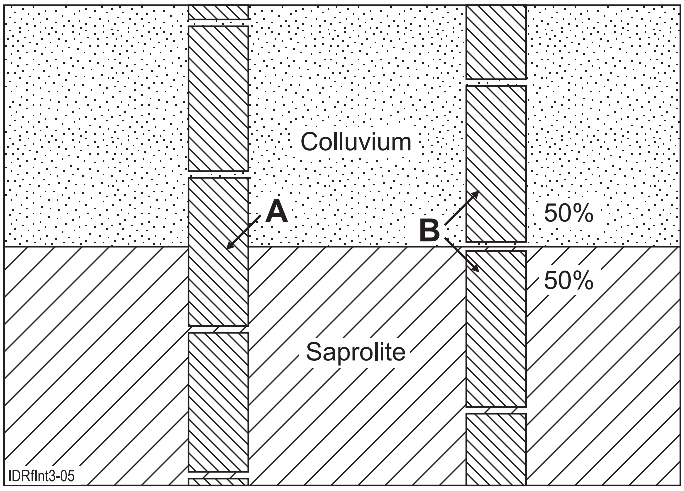

Figure 11. Interface sampling. Where a mixed sample of both sides of the unconformity is available, the appropriate metre interval is selected (A). Where a mixed sample is not apparent (B), a 50/50 mix of metre intervals above and below the interface is selected to ensure the interface is included.

In most circumstances, an aliquot of the whole sample is crushed and pulverized for 'total' analysis. However, in specific settings, particular components, such as ferruginous gravel or mottles, may be separated Selective leach analysis might be appropriate to emphasize active hydromorphic dispersion.

TRANSPORTED OVERBURDEN

DEFINITION, FORMATION AND DISTRIBUTION

Types of overburden

Transported overburden generally refers to exotic or redistributed material of continental origin that blankets weathered and fresh bedrock. In some cases, it is partly cemented by Fe oxides, silica or carbonates. The term usually excludes dominantly marine, lithified sequences in sedimentary basins, that themselves may host mineral deposits, and igneous units such as the Tertiary flood basalts of Victoria, New South Wales and Queensland, that overlie rocks of the Precambrian Shields and Palaeozoic fold belts. Transported overburden commonly refers to: -

- Aeolian clay (parna or loess) and sand, in semi-arid and arid environments.
- Sheet-wash deposits, colluvium and alluvium.
- Evaporites in playas (*e.g.*, halite, gypsum) and palaeodrainage channels (*e.g.*, valley or groundwater calcrete).
- Piedmont fan and outwash deposits of cobbles, gravel, sand and clay shedding from dissected plateaux, hills and mountains.
- Talus and landslip deposits in hills and mountains.
- Sediments in palaeodrainage channels, including sand, alluvial and lacustrine clays, lignite and estuarine sediments.
- Glacial deposits.

The relative timing of continental sedimentation and the principal weathering events have considerable potential significance for exploration. Older sediments are more likely to contain chemical dispersions from concealed mineralization. Those deposited before, during or just after the main phases of deep weathering in the Mesozoic and early Tertiary will have been subjected to more post-depositional alteration (and therefore dispersion) than younger sediments. The principal types of transported overburden and their distributions in the landscape are illustrated schematically in Figure 12.

1. Sediments pre-dating deep weathering

These are commonly difficult to recognize and mainly occur as remnants. Unconsolidated Permian glacial sediments on the Yilgarn and Gawler Cratons are examples; they are commonly strongly weathered, although unweathered sediments may also occur in deep channels (*e.g.*, near Laverton, WA). The Permian glacial deposits merge laterally with contemporaneous continental and marine sediments in adjacent sedimentary basins. Other sediments, such as the Mesozoic outliers on Proterozoic basement in the Mt Isa Block, may also be deeply weathered and potentially contain elements dispersed from underlying mineralization.

2. Sediments broadly contemporaneous with deep weathering

a). Colluvium. Colluvial movement on slopes is a consequence of weathering. Rain splash, mass flow and sheetwash contribute to downslope movement of soil components, even in deeply weathered terrain of low relief. Depending on relief, bedrock geology and maturity of the landscape and regolith, the eroded material will vary from essentially unweathered minerals derived directly from outcrop to intensely weathered minerals such as kaolinite, gibbsite and secondary Fe oxides. The eroded materials may form a minor component of soils on gentle gradients, but tend to accumulate at the base of slopes and in lower parts of the landscape. They become part of the regolith at this new site and an inherent part of the weathering profile. In low-lying parts of the landscape, the regolith may have lower horizons developed in residuum and upper horizons in colluvium. For example, at Mt Keith (*this volume*), the plasmic and ferruginous mottled clay horizons have developed across the residual-colluvial unconformity and have characteristics of both the underlying ultramafic rocks and sediments of felsic origin, due to mixing by post-depositional processes such as slumping and churning.

b). Palaeochannel sediments. Palaeochannels ("inset-valleys" or 'deep leads') have long been recognized in the regolith. They were important early sources of gold in Victoria (*e.g.*, Avoca and Lodden valleys, near Ballarat) and Western Australia (Coolgardie-Kalgoorlie goldfields; Gibb-Maitland, (1919), and continue to be exploration targets (Palaeochannel Au deposits, Mt Pleasant, WA; *this volume*). Numerous palaeochannels have since been found across the continent (*e.g.*, the very large systems on the Gawler Craton). Many mineral deposits (*e.g.*, Bronzewing and Northparkes; *this volume*) are overlain by, or are adjacent to, palaeochannels. The channels are important because they may: -

- Directly overlie and conceal primary or supergene mineralization.
- Host supergene deposits of Au, U, industrial minerals and base metals;

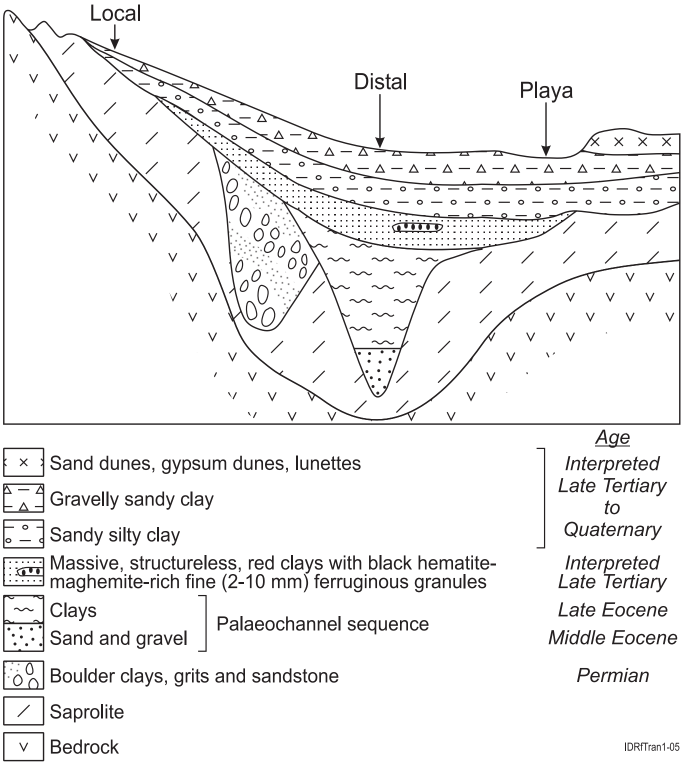

Figure 12. Schematic diagram illustrating the principal types of transported overburden and their distributions in the landscape.

- Contain geochemical or mineralogical dispersion products from mineralization;
- Provide evidence for the age and evolution of the regolith and landscape.

The channels are of different ages and dimensions. The major trunk drainages may be old, perhaps excavated in the Permian or before, and are largely followed by the present systems, although there is evidence for drainage capture and reversal since then (*e.g.*, van der Graaf *et al.,* 1977; Kern and Commander, 1993). However, tributary drainages may follow quite different courses and, although most occur in lower parts of the landscape, some, mostly smaller, channels are in more upland sites (*e.g.*, Mt Percy; *this volume*). Palaeochannels within the present drainage systems remain as aquifers where suitable sediments (*e.g.*, calcrete, sand and gravel) occur.

Many channels in the Yilgarn Craton are steeply incised into pre-existing residual regolith. Some overlie lateritic residuum, others contain detrital pisoliths and nodules in their basal sediments. In addition, the sediments themselves have been weathered since deposition. They have leached lower horizons (saprolite after reduced clay-rich sediments) and strongly mottled upper horizons, locally cemented to form duricrusts, which contain pisoliths formed *in situ* (Figure 12). Unweathered sediments, including lignite and organic clays, remain in some deep channels; palynological dating commonly gives late Eocene ages (Kern and Commander, 1993; de Broekert 2004; Mulga Rock; *this volume*). Thus, the channels and sediments appear to be from a period between two episodes of deep weathering. Similar relationships are apparent in many palaeochannels across southern Australia. The sediments in the channels are described in the chapter on Weathering History (*this volume*).

3. Recent sediments

This last group of sediments is the most widespread and most variable, overlying fresh rock and older residual and transported regolith. The sediments consist of the physical and chemical weathering products of these precursors and occur throughout the landscape, although they are most abundant at lower levels and in floodplains. The principal sediments are (i) colluvium, (ii) alluvium, (iii) aeolian sands and clays, and (iv) evaporite.

These sediments are especially widespread in arid regions; they were derived from increased erosion following the change from more humid climates, in part due to instability from reduction in the vegetation. Certain regolith units have been indurated by irreversible dehydration (lateritic duricrust) or by introduced cements such as silica, Fe oxides and carbonates (silcrete, ferricrete and calcrete). However, much of the regolith is soft, unconsolidated and susceptible to severe erosion by water and wind, even in areas of low relief. Because of the reduced rainfall, much of the drainage is incapable of removing the sediments, which remain in the landscape, infilling valleys, reducing relief further. This particularly applies to inland areas where erosion is to the base level of the playas.

Much of the rainfall in the semi-arid interior is spasmodic but heavy, and excess water runs off as a fairly continuous sheet, washing across the surface. When the uppermost horizons are saturated and soft, run-off increases and becomes erosive. Sheetwash is a dominant erosion and deposition process on surfaces of low relief in all but thickly vegetated regions. The process transports clays, silt and fine sand, even in rainforests; in arid areas, during heavy rainstorms, gravel and small pebbles may be moved across slopes of less than 1°. Fine particles are carried in suspension and coarser fractions as a traction load. Water flow is discontinuous, changing with surface irregularities and rainfall intensity. Networks of braided rills and wash channels can develop and, depending upon the local topography, may converge into larger washes or diverge across flatter depositional areas. Such networks are only temporary and, from season to season, the whole surface is affected. The resultant sedimentary sequence consists of a series of discontinuous beds, mostly poorly-sorted, commonly cross-cut by infilled scours and channels. These sediments are commonly referred to as colluvium (or colluvium-alluvium), and are the most widespread and abundant type of transported overburden in much of the arid interior. Better sorted and mostly finer grained sediments (silty clay and clay), generally associated with more defined drainages and in valley axes and floodplains, are referred to as alluvium. In most arid regions, the surface of colluvial and alluvial tracts is commonly strewn with a polymictic lag and has a thin (100-300 mm, rarely greater than 500 mm) friable soil. The soil may have a relatively higher content of silty clays, particularly in flatter areas in outwash plains, and a minor organic component in the top 100 mm. Red-brown hardpan is ubiquitous across much of the centre of the continent, especially in colluvial-alluvial plains. In hardpan, the matrix and some clasts of the sediment are partly replaced and cemented by hyalite (opaline silica) and alumino-silicates, giving a broadly sub-horizontal, laminar structure with Mn oxides precipitated on partings. Such 'hardpanization' can be from 1 to 10 m thick and affects residual units beneath the transported overburden.

Around playas, alluvium merges with mostly clay-rich lacustrine sediments, which have a strong evaporitic component at the surface, dominantly gypsum and halite. Groundwater or valley calcretes occur as narrow, near-surface lenses, 5-30 m thick, in drainage axes in an area extending from central WA into the NT and SA. Limestones and dolomites also occur deep within the sediments of many palaeochannels. Dominantly sandy aeolian deposits form aprons and dunes over granitic and sedimentary terrain in the arid interior and sand and gypsum (kopi) dunes on the margins of playas. However, there is a significant aeolian component to many soils. The influence this has on soil geochemistry is not commonly considered, but actual and potential dilution is significant, both in semi-arid regions (Beasley Creek, WA; and Nifty, WA: *this volume*) and in more humid regions downwind (Blayney, NSW; Dickson and Scott, 1998; Scott 1999). Some pedogenic carbonates in both residual and clastic transported regolith in the Gawler Craton, SA, probably have a significant aeolian component. These carbonates also act as diluents for most elements, although reworking in the soil permits them to concentrate Au (Lintern, 2002; McEntegart and Schmidt-Mumme, 2004).

Post-depositional modification of these younger sediments is less than in older deposits. However, cementation of surface horizons is widespread in arid regions, *e.g.*, by pedogenic carbonates in the south and silica in the north. Such cementation generally modifies pre-existing regolith, rather than forming specific horizons or units. It can transgress regolith boundaries, including the unconformity between transported and residual regolith. The overall composition thus strongly reflects that of the host material, except for some massive calcretes, in which the carbonate has almost totally replaced or displaced the host matrix.

USE AS A SAMPLING MEDIUM

Although minor colluvial transport during deep weathering contributes to the effectiveness of soil, lag and laterite sampling by broadening the dispersion haloes, transported overburden is rarely an effective sample medium. In regions where bedrock and mineralization are extensively weathered and leached, further dispersion is generally limited to mechanical smearing at the bedrock/overburden interface, as discussed above. Dispersion to the surface is generally precluded in arid regions and it is no coincidence that most mineral discoveries attributed to surface sampling techniques in such terrain have been made on hills and low rises, with outcrop and residual soil, above the overburden-covered plains. Despite extensive testing of different sample media and using a variety of total and partial or selective analytical techniques, there are few unequivocal examples of surface geochemical anomalies being directly related to mineralization concealed by transported overburden. The principal exceptions are some Au deposits in the southern Yilgarn Craton and the Gawler Craton, where hydromorphic Au anomalies occur in calcareous soils and calcrete developed in shallow sediments. Even here, however, carbonate sampling can only 'see through' a maximum of 5-10 m of sediment (Butt *et al.,* 1997b; Lintern, 2002; Kanowna Belle, Safari, Panglo; *this volume*). In comparison, in non-calcareous soils, deposits may be blind where the sediment is only 2 m or less thick (*e.g.*, Fender and Harmony, WA; *this volume*), probably depending on bioturbation as the principal near-surface dispersion mechanism. Deeper bioturbation is possible, but cannot be relied upon. In this context, it can be noted that a surface anomaly is reported from partial analyses of soils at Osborne, Queensland (Osborne; *this volume*: Lawrance, 1999), which is concealed beneath 30-60 m of Mesozoic marine sediments. The metal enrichment of several sub-horizontal zones in these sediments may have occurred during marine depositional-diagenetic stages, or later sub-aerial weathering, with near-vertical fractures as fluid pathways. The soil anomaly possibly reflects one such enrichment zone.

Metal enrichment of younger sediments in palaeochannels has also been recorded. At Dalgaranga (*this volume*), widespread Cu-Zn anomalies in shallow (10-20 m) oxidized clays are probably related to minor sulphide enrichment in the basement, although the direct source is uncertain. At Mulga Rock (*this volume*) U-Cu-Pb-REE enrichment in lignite may represent a favourable trap site rather than a specific source. Zinc and Cu enrichment (to over 250 ppm) in sediments at Portia (*this volume*) appears to be unrelated to the underlying Au mineralization. In none of these cases has a surface (soil) anomaly been detected.

SAMPLING PROCEDURES

Generally, overburden sampling is avoided and systematic grid drilling to residuum is preferred. Exceptions are where the overburden is very thin (<2 m) and, in gold exploration, where pedogenic carbonates occur and overburden is <10 m thick. However, even in such environments there may be uncertainty, since the thickness of overburden may increase without any obvious indication at surface. In both instances, shallow power augering is generally the most appropriate procedure.

In environments where metal enrichment in deeper sediments is anticipated, present or past redox fronts may be specifically targeted during exploration drilling. Such fronts are associated with organic matter and/or sulphides (*e.g.*, lignite, Mulga Rock; *this volume*: Argo; Lintern and Gray, 1995), or Fe oxides. At some sites, the latter may themselves have been derived from oxidized sulphides (Osborne and Dalgaranga; *this volume*). The redox fronts represent trap sites for metal enrichment during sedimentation, diagenesis or weathering.

Where systematic drilling is employed, and especially if it is intended to collect buried lateritic residuum or interface samples, it is essential to be able to distinguish between transported and residual regolith. The following characteristics of transported overburden may be useful.

Sediments

i) Polymictic. ii) Fractured ferruginous fragments. iii) Maghemite at depth - indicates material once at the land surface. iv) No cutans on pisoliths – but pisoliths developed *in situ* in sediment have very well-defined and commonly multiple cutans. v) Weatherable minerals in near-surface. vi) Absence of lithic fabrics – although detrital lithic fragments, *e.g.*, in Permian glacials, may be misleading. vii) Lignite and organic matter. viii) Rounded quartz - especially in basal gravel. ix) Change in resistate mineralogy, *e.g.,* abrupt downward appearance of mica or talc may indicate the basal unconformity.

Sediment sequences

Palaeochannel sequences commonly have massive, structureless clay that is mottled in the upper part, overlying a quartz-rich gravel and sand unit. The latter will be approximately horizontal (distinguishing it from disaggregated quartz veining), have some rounded quartz, attenuate laterally (across channel) and be below the deepest section of the clays. Carbonaceous material may occur in reducing environments and marine sediments, such as spongolites, may occur in estuarine sequences in palaeodrainages and other near-coastal environments.

An 'inverted' regolith stratigraphy, with fine, clay-rich materials overlying ferruginous gravels, may indicate colluvium-alluvium derived from the erosion of a lateritic landscape.

Hardpan (red-brown silica cementation, Mn oxide precipitates on partings) is not an indication of transportation, since this is a modification of pre-existing materials and can affect both residual and transported components of the regolith – although most hardpans are formed in colluvium.

The presence of disordered kaolinite, as detected by infra-red reflectance spectroscopy, may be effective in distinguishing between transported and residual units (Pontual and Merry, 1996). However, the relationship is empirical and is not diagnostic everywhere.

STREAM SEDIMENTS

DEFINITION

Stream sediments are unconsolidated materials that are being mechanically transported in a confined, connected drainage channel by saltation, traction or suspension in flowing water, or that have been chemically precipitated from the stream water; commonly, stream sediments consist of both. The detritus may range from boulders to clay and include both mineral and organic matter. Active stream sediments are those being transported or reworked during stream flow under the present climatic environment – bearing in mind that many streams only flow seasonally or intermittently after rain. Bank or over-bank sediments are those deposited during the waning stages of flood events. Connected drainage is commonly absent from many semi-arid regions of low relief. Following heavy rain, surface water is shed by sheet flow or sheetwash – a more or less continuous cover of flowing water, either unconfined or in broad, ill-defined channels. As described above (Transported Overburden), this process transports clays, sand and gravel across slopes of less than 1°. Water flow is discontinuous, forming networks of braided rills and wash channels that change from season to season. In places, the colluvial sediments deposited by sheetwash may be used as a substitute for stream sediments, but their provenance is generally less certain.

DISTRIBUTION

The principal requirement for stream sediments to be used as a sample medium is uniform dissection of the terrain, so that a high proportion of the region of interest can be represented by sampling. Sampling generally cannot effectively cover major valleys and flood plains. Most of Tasmania consists of dissected areas suitable for stream sediment sampling. Similarly, those parts of the mainland where there is direct external drainage are also suitable. These include much of the Lachlan Fold Belts along the E and SE seaboard, the Kanmantoo Fold Belt and Flinders Ranges, parts of the southern Gawler and SW Yilgarn cratons, and the Gascoyne, Fortescue, Pilbara, Kimberley and Pine Creek regions.

In the interior, some large areas of moderate to high relief, such as parts of the Arunta Block, and smaller, local areas of coordinated drainage radiating from moderately dissected uplands, are also suited to stream sediment sampling. However, there are large regions that have broad, widely-spaced trunk valleys and extensive tracts of transported overburden, with surface drainage that is largely uncoordinated and dominated by sheetwash; other areas have no significant drainage. These cover many important, mineral provinces, including most of the Yilgarn and Gawler Cratons, Curnamona Block and Granites-Tanami Block. The absence of a connected drainage network over these regions has been a major impediment in constructing regional geochemical maps in Australia. In Western Australia, regional surveys using mixed media (stream sediments, colluvium, soil, lateritic pisoliths) have been used in an attempt to overcome this problem (*e.g.*, Morris *et al.,* 1998; Morris and Verren, 2001).

USE AS A SAMPLE MEDIUM

Stream sediment sampling is a well-established procedure for mineral exploration at a wide variety of scales, from broad, province-scale reconnaissance surveys through to local surveys that may indicate outcropping mineralization. Thus, sample densities may vary from one sample per several km^2 to several samples per km^2. The general principles are well described in Hale and Plant (1994), with specific application to arid terrains by Mazzucchelli (1994). At a regional level, surveys may be (1) reconnaissance surveys, for which a representative proportion of streams of a specified (usually low) order is sampled, to identify broad mineral provinces, and (2) regional surveys, in which all streams of a specified order are sampled, to obtain a 'complete' coverage. Stream sediment and loam surveys of heavy minerals for diamond exploration have been conducted across much of Australia. The results of these surveys are generally proprietary and are beyond the scope of this volume.

There have been numerous regional surveys in Australia by industry and government agencies. Much of the early data are based on partial and mixed acid (many without HF) analysis for a limited suite of elements. For example, for the 80 000 km^2 survey of the Halls Creek province WA, undertaken in 1964-1965, samples were analyzed for cold extractable Cu, 'total' Ni, Cu, Pb, Zn and, in places, 'total' As (Halligan and Harris, 1980). More recently, analytical procedures have improved and element suites have increased. Recent regional reconnaissance surveys by the Geological Survey of Western Australia and the Northern Territory Geological Survey are based on total analyses by XRF, four-acid digest and combined ICPMS/OES for 35-48 elements, and fire assay fusion for Au, Pt and Pd (*e.g.*, Morris and Verren, 2001; NTGS, 2002). Compilations of regional survey data have been assembled by exploration companies and State Geological Surveys, and provide a valuable resource (*e.g.*, Beams and Jenkins, 1995, see also Mt Leyshon (*this volume*); NSW-DMR, 2004). However, there are obvious problems in levelling data for samples collected and analyzed by different procedures and at different times.

There are numerous case histories containing stream sediment data. These are from a wide range of climatic and physiographic environments, but the preponderance of information is from the Phanerozoic of eastern Australia. These include examples from the temperate rainforests of western Tasmania (*e.g.*, Que River Pb-Zn deposit, Skey and Young, 1980) to the arid northern Flinders Ranges, SA (Beltana Zn deposit: Moeskops and White, 1980). The data show that, in more humid regions, hydromorphic dispersion may contribute significantly to the anomaly and result in long drainage trains. This is very distinct in the Mt. Lofty Ranges, SA, where environmental disturbance by clearing has led to considerable element mobility, the development of acid sulphate soils and the precipitation of base metals in high concentrations in ferruginous seeps along streams (Mt. Torrens, *this volume*). At Que River, hydromorphically dispersed Zn extends further down drainage (peak >1000 m) than clastically dispersed Pb (peak <400 m) (Skey and Young, 1980). Dispersion trains of similar or greater length occur in other humid environments, such as at the Yandan Au deposit, Drummond Basin, Queensland (*this volume*), the Timbarra Au deposits, NSW (Cohen *et al.,* 1999; *this volume*) and Halls Peak Cu-Pb-Zn-Ag deposit, NSW (*this volume*). At the latter, mine contamination has contributed to dispersion of over 40 km.

In more arid regions, clastic dispersion dominates and drainage trains are generally quite short. At the Oonagalabi Cu-Zn prospec, McDonnell Ranges, NT (*this volume*), there are distinct multi-element signatures, but they do not extend into third order streams due to dilution. Similarly short trains have been recorded from the Beltana willemite Zn deposit (Moeskops and White, 1980), Wonawinta Zn-Pb-Ag prospect, Cobar, NSW (*this volume*) and the Century Zn-Pb-Ag deposit, Queensland (*this volume*). At Century, two uncontaminated 300 km^2 catchments have anomalous Zn contents, but are potentially obscured by regionally high background in Mn-Zn-Pb-Cd derived from apparently unrelated enrichment of partly overlying Cambrian limestone. Stream sediment surveys in these districts (except Century) contributed to new discoveries, but in each case resulted from sampling at close intervals (2 per km^2), generally from streams 2-3 km in length.

Contamination can be a major problem with stream sediment surveys and is mentioned in several case histories herein and other published data (*e.g.*, Halls Peak (*this volume*); Century (*this volume*). Most of the contamination is due to mine tailings, but does not necessarily preclude success. Potential contamination from past mining activities is generally relatively restricted and can commonly be avoided by careful sample site selection and data interpretation. Thus, the Khan's Creek gossan (Palethorpe, 1980) was found despite the general contamination in the Halls Peak area. However, contamination by past exploration activities is both more widespread and more difficult to detect. Sediments from streams in explored areas may contain drill cuttings; these can occur in all size fractions and may include fresh, sulphide-bearing rock fragments as well as weathered material. Results from total and partial analysis will be biased and influence interpretation. Such contamination will affect both detailed exploration surveys and regional reconnaissance surveys aimed at providing baseline geochemical data. For the latter, re-analysis of samples retained from early surveys, such as the Pickands Mather 1964-5 survey of the Halls Creek Province WA (Halligan and Harris, 1980) may be of particular value, as these pre-date much of the drill-intensive exploration of more recent years.

SAMPLING PROCEDURES

Stream sediment surveys are commonly based on sampling first, second or third order tributary streams; higher order streams are commonly too large, causing considerable dilution. The sample density varies according to the application, ranging from 1 per 15-20 km^2 for regional reconnaissance to 3-5 per km^2 for detailed follow-up. Active sediments are collected from close to the centre of the channel, preferably compositing several sub-samples to ensure that the sample is representative. For Au exploration, high energy sand and cobble bars are recommended because, in most stream environments, Au is transported as a heavy mineral and accumulates in the fine fraction (<100 µm) at these sites (Fletcher and Loh, 1996; Melo and Fletcher, 1999). Bank and overbank samples may be used in areas where mine contamination is possible, since these may represent material deposited prior to the commencement of mining.

The whole sample may be used for analysis but, more commonly, one or more specific size fractions are selected. Samples may also be panned to separate heavy minerals. The most appropriate size fraction is best selected following an orientation survey. Thus, the regional survey of the McDonnell Ranges NT (NTGS, 2002) was conducted following the orientation at Oonagalabi (*this volume*). Judicious use of data from appropriate case histories, including those in this volume, may obviate the need for a detailed orientation in some areas. Dilution by aeolian material and the derivation of sediments from strongly weathered, leached rocks are specific problems that can affect the application of stream sediment geochemistry in arid terrains, but these can be combated by selection of appropriate sample fractions, analytical suites and data thresholds.

Commonly, the coarse (>500 µm) or fine (<75 µm) fractions give the best results, because these concentrate Fe oxide rich fragments, and fine clays and oxides, respectively, and exclude much of the aeolian material. The fine fraction may also include widely dispersed heavy minerals, including Au, as noted above. The intermediate fraction may be dominated by aeolian quartz in much of Australia. However, in SE Australia, aeolian material is commonly about 70 µm in diameter in the Cobar district and becomes finer to the east. It is <40 µm in diameter in the Bathurst district, 400 km SE (Tate *et al.,* 2003; Hesse *et al.,* 2003) and so, in that region, coarser fractions are a better sample medium. Partial extraction analysis can be used to distinguish hydromorphically dispersed metals, and has particular application in more humid regions. Bulk Leach Extractable Gold (BLEG) analysis of large, unsieved samples has been applied in an attempt to overcome the 'nugget effect' in sampling and analysis for Au, and to provide a sensitive procedure that can detect widespread dispersion haloes. However, the technique seems to offer no advantages over the <75 µm fraction in much of Australia (*e.g.*, Mazzucchelli, 1994; Yandan, *this volume*; Timbarra, *this volume*).

GROUNDWATER

DEFINITION

Groundwater refers to all sub-surface water. Water in the unsaturated zone above the water-table is referred to as vadose, whereas that in the saturated zone below the water-table is phreatic. Hydrogeochemical exploration uses phreatic groundwater, generally from the uppermost, unconfined aquifer. However, it is not uncommon for drill holes to intersect confined aquifers deep in the regolith, especially in depositional landforms with impermeable sediments. Hydrogeochemical surveys aim to detect elements or their isotopes being actively dispersed from weathering mineral deposits, or from primary dispersion haloes associated with the deposits, with potential to reveal blind mineralization concealed by cover sequences.

A water sample inevitably contains suspended solids. The accepted definition of water is a solution that passes through a 0.45 µm filter (Brown *et al.,* 1970) although smaller filter pore sizes are now being used, hence fine colloidal particles, clays and oxides will remain in the filtrate that is analysed.

DISTRIBUTION

Groundwater can be most readily sampled in areas of moderate to high rainfall, where the water-table intersects the surface at seepages and springs. However, such conditions are relatively rare in Australia, largely confined to near-coastal regions where other exploration techniques are generally more appropriate. The water-table in semi-arid and arid regions is commonly at depths of 5 - >100 m, being close to surface only in playas. Most hydrogeochemical surveys thus depend on sampling exploration drill holes or stock water bores and wells.

USE AS A SAMPLE MEDIUM

Hydrogeochemical surveys are best suited to elements that are relatively soluble in the near-surface environment, with the dominant dispersion mechanism being by groundwater flow. The pH of natural water may range from about 3.5 to 9, so there may be more than one ionic complex species for each element (*e.g.*, for Cu: Cu_2^+, $CuCO_3^o$, $CuCl^+$, $CuSO_4^o$, $Cu(OH)^+$). The dominant species in any given solution is dependent on other solution parameters, especially the concentration of anionic species. Thus, analysis for total element concentrations, rather than ion specific techniques, are preferred (Mann, 1980). Groundwater sampling has also been applied to dissolved gases (*e.g.*, helium: Butt and Gole, 1986), for which upward dispersion as bubbles is possible.

Improved techniques of analysis and data interpretation have made hydrogeochemical surveys more attractive, but there appear to be few examples of such surveys leading directly to mineral discovery. The most significant advances have been increased knowledge (i) at the deposit scale, of the aqueous geochemistry and active dispersion of ore related elements in a variety of different geological, regolith and climatic settings, and (ii), at the district to regional scales, of variations in groundwater composition and solution characteristics and their impacts on the potential application of hydrogeochemical techniques. The greatest emphasis has been placed on Au and U exploration.

Numerous studies on the Yilgarn Craton (Gray, 2001) have demonstrated there to be at least four major groundwater regimes, based on variations in salinity (<0.02 to >30% TDS), acidity (pH 3 – 8.5) and oxidation potential (Eh -200 to >800 mV). These variations have a profound effect on the concentrations of many elements: -

- Al, Li, Y, REE, U: controlled by pH, with high concentrations in acid groundwaters, *e.g.*, in Kalgoorlie region;
- Mn, Co, Ni, Cu, Zn: less correlation with pH and may show lithological variation;
- Cr: correlates with ultramafic rocks, irrespective of pH;
- As, Sb, Bi, Mo, W: low in acid groundwaters, but increase when pH>6.5;
- Au: enhanced concentrations in saline groundwaters, where it forms halide complexes under acid, oxidizing conditions.

The implication for exploration is that Au is the best indicator of Au mineralization in the acidic, oxidizing and highly saline waters of the Kalgoorlie region and other areas, especially in the southern Yilgarn Craton, because of the low solubility of other potential pathfinder elements. This is also the region where the greatest supergene mobility of Au is found, with considerable leaching and depletion in the upper regolith and secondary concentration at depth (*e.g.*, Mt. Percy, Panglo and Rose (Paleaochannel Gold deposits), *this volume*). Carey *et al.,* (2003) found a broad Au anomaly (threshold 11 ppt, maximum 52 ppt) in groundwaters around the Junction Au deposit, St. Ives, extending W to Lake Lefroy, based on sampling on a 1x1 km grid. No other potential pathfinder element indicated the mineralization; any detectable concentrations are proportional to the salinity. However, local hydrological conditions are important, as the nearby Argo and Apollo deposits do not appear to have such a clear signature, especially in deep groundwater in contact with the mineralization (Lintern and Gray, 1995). In the N of the Yilgarn Craton, most groundwaters are neutral and fresh, and only become saline in valley axes, and concentrations of dissolved Au are two orders of magnitude less (*e.g.*, Cox-Crusader, *this volume*; Harmony, *this volume*), so that thresholds are significantly lower. Conversely, As, Sb, Bi, Mo and W are more soluble and can be used as pathfinder elements. As a consequence of lower Au mobility in these areas, leaching and supergene concentration of Au are also generally minor. Similar groundwater regimes are evident in the Gawler Craton, with similar implications for supergene Au mobility and hydrogeochemistry (Gray *et al.,* 2001).

Regional variations in groundwater geochemistry have also contributed to the distribution of calcrete U deposits in WA and NT. These are deposits of carnotite ($K_2(UO_2)_2 V_2O_8.3H_2O$), associated with waters of low to moderate salinity in valley axes in the northern Yilgarn Craton and similar environments to the N and E, having dominantly granitic bedrock (Butt *et al.,* 1977; Butt, 1988). They do not occur in the southern Yilgarn, where the waters are saline and more acidic, possibly due to lower V solubility. A groundwater survey of a 65 000 km^2 region of the northern Yilgarn Craton, centred on the Yeelirrie deposit, based on 575 samples, mainly from stock bores and wells, show a good correlation between hydrogeochemical data, geology and mineralization (Cameron *et al.,* 1980). Drainages with carnotite mineralization were characterized by groundwater containing 100 ppb U, compared to background values of <5 ppb in catchments over greenstones and Proterozoic sediments, and <20 ppb on granitic bedrock. However, within many calcrete drainages, some carnotite deposits are dissolving whereas others are actively precipitating, so that U content alone cannot be used as a predictive vector. Protocols based on groundwater sampling, determination of pH, K, U and V concentrations and calculation of carnotite solubility indices have been developed for hydrogeochemical exploration to indicate dissolution sites up-drainage and the proximity to precipitation sites down-drainage (Mann and Deutscher, 1978; Deutscher *et al.,* 1980a).

In the Alligator Rivers area, NT (*this volume*), high grade U mineralization in veins at Nabarlek, Ranger and Koongarra is indicated by the concentrations of dissolved U, but similar or higher concentrations occur in waters from barren felsic lithologies. Base metals associated with the mineralization give no response, although false anomalies can be derived from sulphidic schists (Deutscher *et al.,* 1980b). However, 'normalized Mg' (NMg = Mg/(Mg+Na+Ca+K) provides a geochemical indicator, increasing towards mineralization, with high values (NMg >0.8) coinciding with high U concentrations and reflecting the association of Mg-chlorite with U minerals. Koongarra is also the only site where dissolved He concentrations are directly related to U mineralization (Gole *et al.,* 1986; see also Alligator Rivers Uranium deposits, *this volume*). Elsewhere, He concentrations appear controlled by hydrological conditions, such as residence time and permeability of the upper aquiclude (Butt and Gole, 1986).

Hydrogeochemical surveys have their greatest potential where mineralization is concealed by transported overburden or other cover materials. In the Lachlan Fold Belt of NSW and Victoria, extensions from known mineralization are concealed by sediments of the Murray Basin and Mesozoic and Cainozoic sediments and volcanic rocks. Groundwater compositions may directly indicate mineralization or the host sequences using specific elements, element ratios and calculations of theoretically saturated minerals (Giblin, 2003). For example: -

- Au, As, possibly with Cu, U, Pb, Rb, Mo: associated with Au mineralization in the Stawell, Ballarat and Bendigo regions, with samples distant from known mineralization indicating potential;
- U, Mo: felsic igneous (probably granitic) rocks that host Mo deposits, near Bendigo;
- normalized Mg (see above): a guide to mafic Cambrian volcanic rocks that host Au mineralization in Victoria;
- modelled minerals: may indicate bedrock sequences associated with gold (muscovite±talc, antigorite) and base metal (witherite) mineralization, or calcic (strontianite) or ultramafic (talc, antigorite) rocks.

Water from cover sequences may, however, dilute these responses, and other indicators, such as isotopic ratios, may be necessary to identify the chemical signature of basement rocks. In Victoria, for example, Sr isotopic ratios appear to distinguish Cainozoic basalts from prospective mafic units beneath (Giblin, 2003). At Abra, Western Australia, mineralization can be detected in groundwaters by distinctive Pb, relatively high S and high Sr isotopic ratios (Whitford *et al.,* 1998). A distinctive S isotopic ratio occurs in waters up to 1 km from the blind Menninnie Dam base metal mineralization, Gawler Craton (Andrew *et al.,* 1998). Similar studies in the Broken Hill region have recognized that some variations in S, O, Pb and Sr isotopic ratios can be attributed to contributions from oxidizing Pb-Zn-Ag mineralization and its host rocks (Caritat *et al.,* 2003, 2005; Kirste *et al.,* 2003).

Direct contact with mineralization and pervasive distribution mean that groundwater is an attractive sample medium for exploration for concealed mineralization. Nevertheless, despite the promise shown by results such as those discussed above, much work remains to be done before hydrogeochemical surveys can be used with confidence. It is essential to have a good knowledge of the chemistry and hydrology of specific regions to interpret data, hence considerable preparatory work is required to optimize the approach.

SAMPLING PROCEDURES

Except where it can be collected directly from seeps and springs, groundwater is sampled from exploration drill holes and water bores. Ideally, holes should be cased with PVC tubing slotted at regular intervals, samples taken at several depths by pump, with packers above and below to avoid mixing waters from different aquifers, and the pump run for some while to ensure the sample is fresh. Such a procedure is impractical in an exploration context for many reasons. Most hydrogeochemical surveys use standing water from open exploration holes and stock bores and wells (Cameron *et al.,* 1980; Gray, 2001; Carey *et al.,* 2003; Alligator Rivers Uranium deposits, *this volume*). Many drill-holes will be uncased, whereas others may be cased, slotted throughout or at some specific depth, or unslotted, so that water only enters from the bottom. It is generally not feasible to pump holes and only sample the recharge because of the small diameter of many holes, the risk of loss of the pump in uncased holes, pump damage by solids, slow pumping/recharge rates and bias towards the most active aquifers. Although the water in an open hole will differ from that in an enclosed aquifer, it is assumed that they will be in dynamic equilibrium; certainly, depth profiles from both uncased and slotted, cased holes show the water to be stratified (*e.g.*, in pH, Eh and salinity). Direct contact with the atmosphere affects the upper part of the water column, and distinct degassing trends are observed for He (Butt and Gole, 1986), so that it is best to collect samples at fixed depths (at least 5 m) below the water-table. Samples are generally collected with a 'bailer'; the most effective is one which has a small pump at the base which is turned on at the specified sampling depth to purge and fill the sample chamber above, and then switched off before being retrieved. This ensures that the sample comes from a known depth. Effective sample densities at regional scales may be as great as 1 sample per 170 km^2 using stock bores (Cameron *et al.,* 1980), whereas for tenement scale exploration, specifically drilled holes on 0.5 to 4 km grids may be needed (Carey *et al.,* 2003).

After retrieval of the bailer, a procedure such as the following is recommended (Gray, 2001). Temperature, pH, Eh and conductivity are determined at the time of sampling. Samples for HCO^{3-} analysis are collected by overfilling a bottle to remove all air before sealing. A further 1.5 L is filtered in the field: 100 ml is acidified for later analysis by ICP-OES and ICP-MS, 50 ml is kept for analysis for Br, Cl and other anions, 1 L is used for Au analysis by shaking with a 1 g sachet of activated carbon in an acid/saline medium (quantitative to <0.005 µL^{-1}). Acidification is recommended to stabilize the solution and prevent precipitation/adsorption of dissolved metals. However, it is essential that the water is filtered first, so as not to dissolve particulates. Filtration at 0.45 µm may be preferable over 0.2 µm, because the latter may remove a higher proportion of colloidal particles. Highly saline solutions require specific analytical treatment, commonly with higher detection limits. Data interpretation requires calculation of the solution species of many major and trace elements, and the degrees of mineral saturation in terms of the solubility indices from the compositions of the solutions.

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