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Phyto-exploration in arid subtropical, arid mediterranean and tropical savanna environments: Biogeochemical mechanisms and implications for mineral exploration

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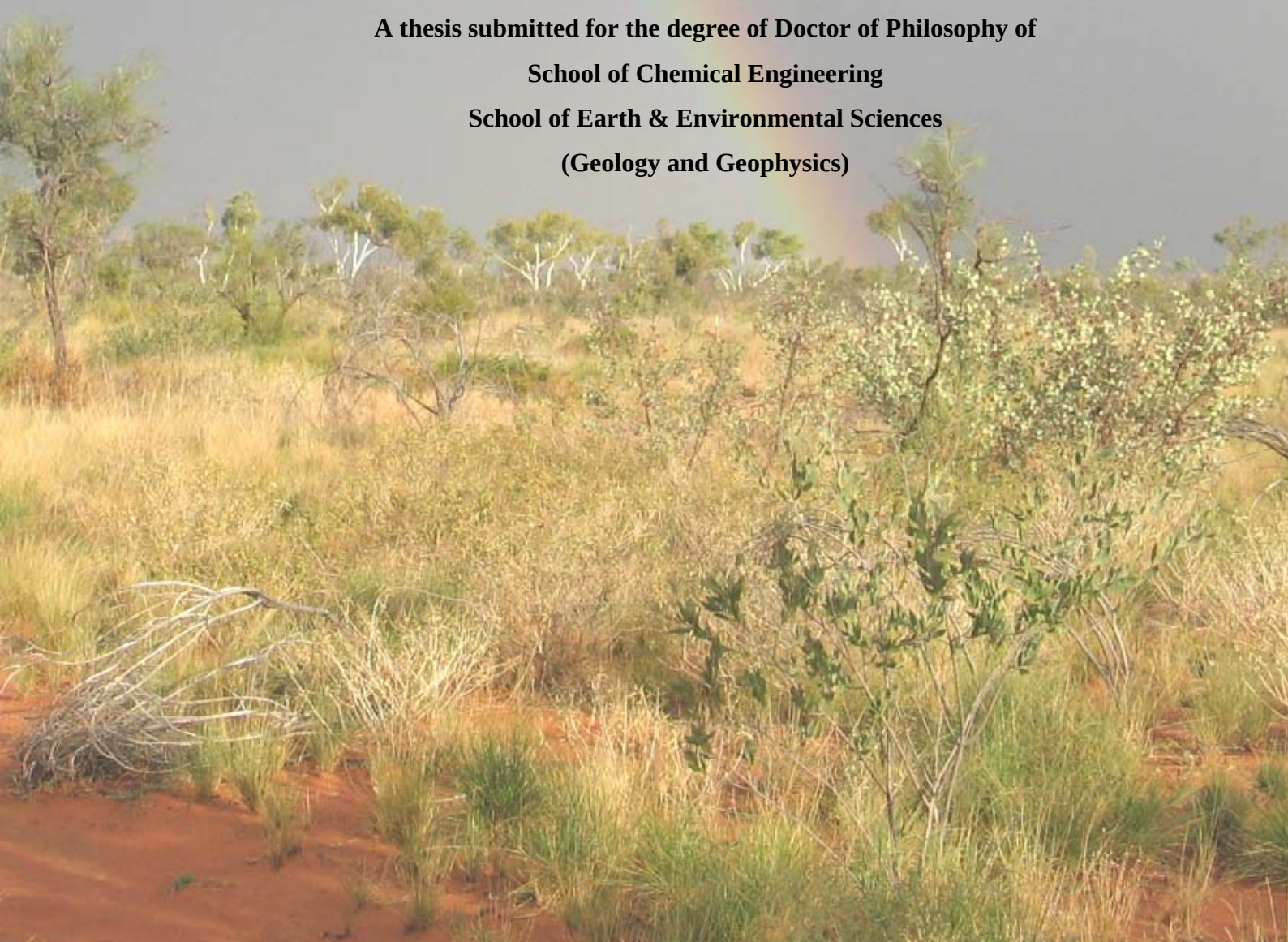

1 Introduction

The search for new mineral resources is hampered by transported cover and the lack of low-cost, developed methods which can be applied by exploration companies. Biogeochemistry is one method that has been applied in many terrains and climates which can be used to identify mineralisation signatures. There is a need to refine this process to sampling several species over small-scale surveys which can be presented as an applied form to mineral explorers. Within Australia there have been few plant species that have been investigated for this purpose and there has been little progress into adapting this methodology into quick orientation programs which exploration companies can use to survey their tenements.

The blanket of soil, sediment and weathered rock known as the regolith can cover and conceal underlying mineral deposits, and therefore has impeded mineral explorers. The aim of this research was to investigate geobotanical and biogeochemical methods in various regions in Australia (Tanami, Pine Creek and Gawler Province, Figure 1.1) to assess their ability to explore through this cover. Biogeochemistry when used as a mineral exploration technique includes using the chemical characteristics of samples derived from living organisms to test for the expression of mineralisation within the local environment.

Figure 1.1: Tanami, Pine Creek and Gawler Regions locations within Australia.

The main focus of the research was on 9 orientation-style studies over or near known Au deposits. The main goals here were to deteremine:

- vegetation associations over known mineral deposits;
- the chemical characteristics of vegetation in relation to geology and regolith materials;
- relationship between different plant species and depth within the regolith profile and whether predictions could be made about regolith stratigraphy; and,
- developing vegetation sampling as an effective and efficient mineral exploration tool (phyto-exploration).

The biogeochemical method is the use of chemical assays of organic matter (vegetation in this case) to determine information about the underlying substrate. Vegetation chemistry has been

investigated in many different terrains and climatic conditions for the purposes of mineral exploration. It has been effective at detecting 'buried' mineralisation targets and has been used extensively in Canada (Dunn 2007), Russia (Malyuga 1963; Kovalevsky 1987), and others (Cole *et al.* 1968; Brooks 1972; Brooks *et al.* 1995; Lintern *et al.* 1997; Cohen *et al.* 1999; Reid *et al.* 2008; Reid *et al.* 2009). Most of these studies have focused on a single detailed study where many samples are collected, with only few plant species being examined. While this has improved the accuracy of the analytical techniques and proven the validity of the method, the problem is that for most areas and mineralisation styles there is a lack of basic knowledge about individual species dominant in different areas (background chemistry, rooting structure and depth), and the important 'pathfinder' elements are generally unknown.

Plant biogeochemical sampling has both economic and environmental applications. Conventional mineral exploration uses drilling to sample buried substrate. This is a very expensive and time consuming process. Also a drill rig needs to access the area which means clearing roads or tracks of trees and shrubs. This is not always desirable in some environmentally or socially sensitive areas. Plant sampling, however, is a low impact medium which does not disturb a site significantly.

The high prospectivity but lack of exploration success associated with covered areas demands that other mineral exploration techniques be developed. One approach to develop is to provide a surficial chemical expression of mineralisation buried by transported regolith. The transported cover often contains geochemically barren or complexly dispersed geochemical expressions of underlying mineralisation. In such settings plant chemistry has the potential to become a useful exploration tool. Conceptually some plants growing in semi-arid and arid regions may have deep root systems that can penetrate the transported cover and carry geochemical expressions from depth, through the roots and into the surficial plant organs. However, it is not necessary that the roots penetrate the transported material, they could also take up elements that have been derived from the underlying mineralisation which have moved up through the profile by other mechanisms.

The Tanami region of northern Australia is highly prospective for Au mineralisation. It hosts the world-class Callie Au-deposit (Cross *et al.* 2005) and other smaller deposits and prospects. Mineral discovery has been restricted mostly to areas of exposed bedrock or their immediate margins. Traditional exploration techniques in these covered settings have mostly involved sampling soils, shallow drilling or geophysical techniques. There have been no previous reports of the use of plant biogeochemical techniques applied in this region.

The Pine Creek Orogen hosts significant Au mineralisation, however most previous mineralisation discoveries are associated with areas of exposed or shallow sub-cropping bedrock (T. Ireland, pers. comm. 2007). Areas with significant transported regolith, in particular the shallow transported regolith associated with the 'black soil plains' have been a major challenge for previous exploration programs, and have been host to limited exploration success. This thesis includes the results of analytical work carried out on vegetation samples taken from the Johns Hill, Great Northern, Glencoe and McKinlay Prospects in December 2006.

The Gawler Craton is a region of significant mineral exploration interest within South Australia. There have been several significant deposits found (Challenger, Prominent Hill and the world class Olympic Dam) with a great amount of exploration still underway. There are vast areas of shallow to deep cover materials that have hindered usual mineral exploration techniques and so other methods (geophysics and calcrete sampling) have been employed

successfully in this area. This study shows the results of analytical work carried out on *Triodia irritans* samples taken from the Tunkillia Prospect in April 2007.

This thesis will present results from 9 small-scale orientation studies over or near known Au deposits (Coyote, Larranganni, Titania, Hyperion, Johns Hill, Great Northern, Glencoe, McKinlay and Tunkillia prospects). Since the sampling was carried out, the Coyote prospect has become an open-cut mine which has provided additional information about substrate. The Hyperion and Pine Creek prospects were 'blind' targets, where nothing was known about the area except that there was Au mineralisation present. Key species and important 'pathfinder' elements will be identified for further exploration potential. Also the feasibility of using small-scale biogeochemical sampling programs for tenement surveys will be presented.

2 Biological and Geological Background and Linking Techniques

In order to understand what plant species were chosen to sample at each of the field sites, and the emphasis on components of the results, it is necessary to follow the background of the plant biogeochemical methodology.

The associations between plants and the underlying substrate have been recognised since the mid-16th century but particularly since the early 19th century, where some plants have been used as indicators of mineralised substrate (Skertchly 1897; Cole 1965; Brooks *et al.* 1995). The work of Georgius Agricola from 1556 recognised the importance of landform on mineral exploration. He showed that there were four main types of landscape that influenced how mineralisation would be expressed: mountains, hills, valleys and plains (Hoover & Hoover 1950).

In geobotany, plant communities have been linked to rock types to aid in geological mapping techniques (Cole 1967; Petts & Hill 2004). A challenge for this is that many of the regions under consideration for mineral exploration have been heavily grazed, which directly affects the expression of vegetation communities (Hill 2004). Regardless, the approach has potential applications for detecting lithogeochemical differences that still interact with the landsurface.

The biogeochemical method involves the chemical assay of living organisms to determine information about the underlying substrate (Brooks *et al.* 1995). Since all plants require a range of elements (macro, micro-nutrients, and trace elements; Kabata-Pendias & Pendias, 1984) and these are generally derived from the substrate in which they are growing; the chemical analysis of plant matter can provide valuable information about the source of these elements. Vegetation can take up elements not required for plant growth in several ways including: inadvertent (passive) uptake, or active uptake for the purposes of metal tolerance, drought resistance, interference with other plants, and pathogen/herbivore defence (Brooks *et al.* 1995; Brooks 1998). Biogeochemical exploration methods have benefits such as: being relatively low cost (especially compared to drilling); providing a relatively homogeneous sampling medium for a given site; being conveniently accessible across wide areas; and, minimal environmental impacts and remediation costs for sampling sites (Brooks *et al.* 1995; Dunn & Ray 1995; Hulme & Hill 2003). The major limitation to this approach however has been a poor foundation of trace element knowledge for different plant species, especially in Australia (Hulme & Hill 2003).

2.1 Geobotany

Geobotany involves the recognition of substrate controls on vegetation distribution (Hall *et al.* 1973). The first step in finding geobotanical associations is plant mapping (Cole 1965; Brooks 1998). This allows for comparing the distribution of vegetation communities with geological features, and may then extend to identifying prospective settings for mineralisation (Cole 1965). Broad observations can sometimes be sufficient as some differences in plant communities are obvious (Brooks 1998). Some plant communities can be directly related to underlying rock types, such as serpentine floras (Cole 1965; Prasad 2005). This can be used even if the underlying rock is masked by regolith materials (Cole *et al.* 1968). A limitation of this work has been that little research has been carried out in tropical regions (Baker & Brooks 1988). There are, however, not always direct links between the plants and substrate, especially in broad and uniform plant communities (Hall *et al.* 1973). One of the benefits is that much of the plant community recognition can be performed with remotely sensed data (Landsat or SPOT), such as occurred over the Thalanga Zn-Pb-Cu mineralisation in Queensland (Cole 1991). In this case, *Eucalyptus affin. polycarpa* grows over the mineralisation and is not present away from it, subsequent leaf analysis showed high levels of Zn (Cole 1991). Another benefit of geobotanical surveys are that they are very cheap and can easily compliment other geochemical or geophysical surveys (Nicolls *et al.* 1965a).

Landforms must also be considered within geobotanical studies because different plant communities can grow on different landforms, which can be independent of underlying structure or chemistry (Brooks 1998). Species can also be restricted by rainfall, climate and soil types (Cole 1965). For example *Acacia aneura* grows in areas with higher water content, this can help in locating shallow groundwater but cannot be related to geological structures directly (Cole 1965). Different species of *Eucalyptus* have been linked to different subsurface geological components (Cole 1965). Some of the first geobotanical associations (noted by Georgius Agricola) was that if an ore body was ‘too hot’ then plants will be small and pale, they could be a different colour, have cracked trunks or generally look sickly from having ‘cooked’ roots (Hoover & Hoover 1950). Certain herbs or fungus were shown to grow over veins but not in any other areas (Hoover & Hoover 1950). This is one of the earliest documented usages of the geobotanical method (Hoover & Hoover 1950). Following this, it was established that plants develop both physical and chemical associations with subsurface materials (geology or regolith) (Malyuga 1963; Cole *et al.* 1968; Brooks 1972; Kabata-Pendias & Pendias 1984; Brooks 1998; Hill 2002; Hill & Hill 2003; Hill 2004; Petts & Hill 2004; Dunn 2007).

One of the earliest recognised geobotanical associations in Australia is related to the ‘copper plant’ *Polycarpaea spirostylis*, which has been shown as a useful indicator of high levels of Cu in northern Queensland (Skertchly 1897; Correll & Taylor 1974; Brooks & Radford 1978). This species attracted a lot of attention as it only grew close to Cu mineralisation or watercourses downstream of a Cu-lode (Skertchly 1897; Correll & Taylor 1974). An example from Western Australia is the Ni hyperaccumulator *Hybanthus floribundus* which has been used in some cases as an indicator for Ni-rich soils (Cole 1973; Brooks *et al.* 1995; Brooks 1998). This can be misleading as hyperaccumulator species concentrate elements within the plant, but the level within the soil does not have to be significantly high. In the Bulman-Waimuna Springs area, there is a change in vegetation assemblage over the Pb-Zn anomaly apparently controlled by metal toxicities (Cole *et al.* 1968).

In the Dugald River area, *Eriachne mucronata* replaces *Triodia pungens* where soils have high concentrations of Zn, Pb and Cu (Nicolls *et al.* 1965a; Nicolls *et al.* 1965b; Cole & Smith 1984). The association surrounding this area is dominated by *Eucalyptus brevifolia* and *Triodia pungens* (Nicolls *et al.* 1965a). *Eucalyptus brevifolia* is the first species to

become scarce with increasing metal concentrations, followed by *Triodia pungens* (Nicolls *et al.* 1965a). It was noted that this association is also associated with ridges and skeletal soils derived from siliceous rocks (Nicolls *et al.* 1965a). This means that follow-up testing of these areas is required to determine if there is an ore body, a change in soil type or whether the elevation changes in the area are significant enough to influence the distribution.

These indicator assemblages can occur for several reasons, such as some plants can restrict their elemental uptake more efficiently than others, or some plants can accumulate the element and are able to tolerate higher levels (Cole & Smith 1984). The 'copper plant' is an example of a species that is able to restrict elemental uptake of Cu (Brooks & Radford 1978). Often indicator species tend to be unpalatable to stock (especially if they are accumulators) and hence reinforce the visual recognition of the change in community (Nicolls *et al.* 1965a). These species are often obvious and visible from detailed satellite imagery and the greatest potential with this field in the future is using remote sensing data to identify the vegetation indicators of mineralisation (Brooks *et al.* 1995).

2.2 Biogeochemistry

Biogeochemistry utilises the chemical composition of living matter to interpret links to underlying substrate chemistry and in particular to detect ore bodies by either direct methods or the identification of dispersion patterns (Cole 1965; Davy & Ryall 1980; Hulme & Hill 2003). Anomalous concentrations of elements associated with mineralisation have been seen in biogeochemical sampling in a variety of locations and mineralisation styles (Debnam 1955; Malyuga 1963; Cole 1965; Nicolls *et al.* 1965; Cole 1967; Cole *et al.* 1968; Brooks 1972; Groves *et al.* 1972; Cole 1973; Hall *et al.* 1973; Brooks & Radford 1978; Cruickshank & Pyke 1986; Watters 1988; Brooks *et al.* 1995; Dunn & Ray 1995; Marshall & Lintern 1995; Lintern *et al.* 1997; Brooks 1998; Cohen *et al.* 1999; Hill 2002; Hulme & Hill 2003; Hill 2004; Dunn 2007). The appeal of this sampling method is a combination of: its low cost of sampling and analysis; it can target a relatively homogeneous medium across wide areas; and, requires minimal remediation costs after sampling (Hulme & Hill 2003). It has particular application where rock is covered by barren or heterogeneous materials, such as sandstones or transported cover materials where traditional soil sampling can be unsuitable (Cole 1965; Hall *et al.* 1973; Rattigan *et al.* 1977; Baker & Brooks 1988; Dunn & Ray 1995; Lintern *et al.* 1997; Cohen *et al.* 1999; Hulme & Hill 2003; Hulme & Hill 2004). Biogeochemistry has been extensively used and tested in Russia (all early work before 1970) and in Canada (since 1960s) where the widespread distributions in areas of low species diversity made them ideal sampling media (Timperley *et al.* 1970; Brooks 1998; Cohen *et al.* 1999). Australia is complicated by having greater species diversity than most of the northern hemisphere (Lintern *et al.* 1997; Cohen *et al.* 1999). Exploration programs in Australia have tested biogeochemical methods since the 1960s where *Acacia aneura* and *Acacia linophylla* were potential indicators of near-surface mineralisation above shallow deposits (Rattigan *et al.* 1977). However, these early studies were restricted by: 'traditional' ideas of geochemical sampling; complexities in interpreting data; mixtures of species over a site; limitations in the analytical techniques; and, poor statistical rigour (Timperley *et al.* 1970; Cohen *et al.* 1999; Hulme & Hill 2003).

Several factors are of great importance when sampling vegetation. The plant species must be widely distributed and have a suitable root structure (Davy & Ryall 1980; Hulme & Hill 2003). Different plant organs contain different concentrations of elements, so consistency is essential (Davy & Ryall 1980; Dunn & Ray 1995; Lintern *et al.* 1997; Brooks 1998; Hulme & Hill 2004). The age of the sampled plant must be relatively consistent, and the organ sampled must be healthy, as insects, bacteria or fungi can alter the chemical structure of the medium

(Lintern *et al.* 1997; Brooks 1998). Seasonality can influence the chemical structure, especially the water uptake of the plant, which can dilute other elements in a wet period and concentrate them in a dry period (Cole *et al.* 1968; Cruickshank & Pyke 1986; Lintern *et al.* 1997; Brooks 1998; Cohen *et al.* 1999; Hulme & Hill 2004). Landscape setting greatly contributes to the plant chemical characteristics, as plants growing in drainage channels often have higher elemental concentrations than those in adjacent settings (Lintern *et al.* 1997; Cohen *et al.* 1999). This may be because of the increase in water leading to increased uptake and/or the channels having higher concentrations of elements due to them being collection areas. Large trees have often been the plants considered for biogeochemical surveys as it is assumed that they have the largest and deepest root systems and hence would provide the greatest direct contact with buried mineralisation (Cruickshank & Pyke 1986; Dunn & Ray 1995). Biogeochemical signatures are also often spatially larger than lithogeochemical haloes (Dunn & Ray 1995). This is due to the movement of elements within the subsurface before reaching the plant roots (Dunn & Ray 1995).

Biochemical uptake mostly occurs through plant roots (Hulme & Hill 2003). Metal ions are exchanged for H^+ ions at the root tips; since the root exudates produced induce a weak atomic charge and are acidic (Kabata-Pendias & Pendias 1984; Hulme & Hill 2003). The activity of soil exudates are increased by low soil temperatures, low water availability, plant injury and micro-organisms (Stanton 1988). The elements are either solubilised out of primary minerals or extracted from groundwater solutions. The elements are then transported to the aerial portions such as leaves (Shacklette *et al.* 1970; Brooks *et al.* 1995; Brooks 1998; Hulme & Hill 2003). Extensive root systems have the potential to penetrate through transported cover which may have heterogeneous chemical signals and may provide a homogeneous signal of the heterogeneous materials (Dunn & Ray 1995; Hulme & Hill 2003). Some cells have electropositive charges that can be used to attract silicates, which in turn can aid in binding other elements to the structure (Brooks 1998). The presence of significant amounts of some elements can enhance the uptake of others, for example Cu uptake is enhanced by the presence of Mo, or Ca increasing the tolerance for other elements (Cole 1965; Nicolls *et al.* 1965a). Whereas the presence of carbonate in significant quantities can suppress the mobility of many elements (Hall *et al.* 1973).

Plant roots seek out areas of high nutrient concentrations and adequate water supply (Hall *et al.* 1973; Stanton 1988; Schenk & Jackson 2002). In the Tanami and other semi-arid regions the water and nutrient availability to the roots is dependant on factors such as: the plant species and its root structure; the local environmental conditions; and, competition from adjacent plants (Schenk & Jackson 2002). In these environments, plants are expected to have greater root to shoot ratios (Cole *et al.* 1968; Hall *et al.* 1973; Stanton 1988; Schenk & Jackson 2002). Plant roots may go many 10s of metres deep to reach a reliable water source (Stanton 1988; Schenk & Jackson 2002; Petts & Hill 2004), which may coincide with penetration of the transported cover to reach underlying bedrock. In such cases deep rooted plants give a more reliable subsurface chemical signature than shallow rooted plants (Debnam 1955). In general, tall trees like *Eucalyptus* are assumed to have deep sinker roots that should give a strong depth signal, whereas small plants like saltbush species are assumed to have shallow lateral root systems (Lintern *et al.* 1997). However, this is not always the case as shown by roots of *Triodia pungens* in the Tanami Region, which were seen at 30 m depth (Reid *et al.* 2008). This is also affected by the rainfall in an area, as desert plants have less than $1/10^{th}$ the root mass of equivalent plants in temperate areas (Stanton 1988). The root turnover rate is also much greater in areas with higher rainfall, from 35% in desert areas up to 97% in tropical regions (Stanton 1988). This has implications for bioturbation and how long it would take for a deep sourced geochemical signal to express itself at the surface.

There are 16 known essential trace elements for living organisms: Fe, Cu, Mn, Zn, Co, I, Mo, Se, F, Cr, B, Li, Sn, Ni, V, and Si (Kabata-Pendias & Pendias 1984; Rashed 1995). Elements that are assumed to be taken up passively are: Al, Sb, Hg, Cd, Ge, Rb, Ag, Au, Pb and Ti, and are found in variable concentrations in plants (Kabata-Pendias & Pendias 1984; Rashed 1995). Some of these elements have been shown to have minor roles in living tissues but the amounts present are low (Kabata-Pendias & Pendias 1984). Different elements are concentrated into different plant organs based on what use the plant makes of the element (Brooks *et al.* 1995; Dunn & Ray 1995). Wood typically contains higher concentrations of Cu, Pb, Zn, Fe, Ni, Ba and Cd (Russell & Van Moort 1981). Bark is generally elevated in Mn, and leaves elevated in Pb, U and Fe (Debnam 1955; Russell & Van Moort 1981). Leaf litter shows close correlations with soils, making them less suited as an alternative to soil sampling (Russell & Van Moort 1981). The concentrations of elements in plant matter is determined by: the concentrations in the subsurface; how much of this is bioavailable; the plant's metabolism; the plant's root structure; the age of the plant; and, climatic conditions (Cruickshank & Pyke 1986). Some elements are often directly linked to substrate minerals, for example Rare Earth Element (REE) concentrations (such as Ce and La) and if these are correlated with P it can show that the plant derives such elements from primary monazites (Cohen *et al.* 1999).

Several elements are classified as toxic to living organisms (e.g. As, Pb, Cr, Cd, Hg, and Al), all of these are tolerable in minor concentrations but eventually lead to cell damage and death (Rashed 1995). Toxicity of these elements is an important factor for what concentrations of the element will be taken up. Some plants exert 'barrier' mechanisms that restrict the uptake of toxic elements (Brooks *et al.* 1995; Cohen *et al.* 1999). Arsenic is considered a highly toxic element, however, some plants growing in elevated As conditions will actively remove it from groundwaters and soils (Brooks 1998). This is enhanced by higher P contents, which aids complexing and increases plant activity (Brooks 1998). Micro-organisms are of particular importance in these cases, while bacteria and fungi are good at either volatilising elements or converting toxic elements into bioavailable forms (Stanton 1988; Brooks 1998). One of the consequences of this can be enhancing the toxicity of elements. In contrast Cr uptake is reported to be restricted in all plant species studied (Cole 1973).

Micro-organisms are very important in biogeochemical studies, as some bacteria can mobilise Au, and algae and other micro-organisms can bind many elements. They are even thought to be important in the formation of some ore deposits (Reith 2003). Similar to geobotanical methods, specific species of microbes have also been found to associate with mineral deposits (Reith 2003). They have also been found to great depth, up to 4.5 km for some bacteria, which increases their potential in exploration (Brooks *et al.* 1995).

Gold is one of the more difficult elements to transport into plant tissues since it is not essential for plant growth (Shacklette *et al.* 1970). However, it has been noted that biogeochemical methods have been more successful in detecting Au mineralisation than stream sediments (Cohen *et al.* 1999). Gold values in plants were first reported by Malte-Brun in 1824 (Shacklette *et al.* 1970). There typically needs to be an increase in solubility and mobility of Au from solid Au within the substrate. Gold complexes are the most efficient method for moving Au to plant tissues. This has been shown from laboratory studies to be passive and more easily performed by Au-cyanide or Au-thiosulphate complexes (Shacklette *et al.* 1970). One potential method is with cyanogenic decomposition, where solid Au is converted into Au-cyanide complexes. This is the most readily absorbed form of Au (Shacklette *et al.* 1970), and there is little documentation of cyanogenic plants and micro-organisms in Australia. Gold can reach the plant root system from weathering of the primary ore which can produce various Au ligands depending upon the host rock composition, once the Au is released into solution from the host, various mechanisms can transport the Au from

the ore body at depth to the active root zone (Shacklette *et al.* 1970; Reith 2003). Often the Au content of the plant is directly proportional to the amount in the soil at the depth the roots are sampling from (Brooks *et al.* 1995). Gold is accumulated in greater amounts from waters, and it has been shown that sea urchins, sea stars and crabs can accumulate Au directly from water and plants growing in swampy ground or water (carrot family, T*ypha spp.* and E*questrium spp.*) can accumulate Au (Shacklette *et al.* 1970; Hosea *et al.* 1986; Lintern *et al.* 1997; Gardea-Torresdey *et al.* 2002; Nakajima 2003; Reith 2003).

2.3 Hyperaccumulation

Hyperaccumulator plants are able to take up elements from soils to levels far above that which is expected (Brooks *et al.* 1995; Anderson *et al.* 1997; Brooks 1998; Prasad 2005; Dunn 2007). There are 2 described cut-offs before a plant is classed as a hyperaccumulator. The plant can either have an elemental concentration above 1000 ppm, or the concentration in the plant must exceed the concentration of the soil (Brooks *et al.* 1995; Brooks 1998). A possible explanation for why some plants are able to hyperaccumulate elements is for defence against predators, insects or fungal infections (Prasad 2005).

Often with hyperaccumulators there is a poor correlation between the concentration of an element in the subsurface and the concentration in the plant (Brooks 1998). This is due to hyperaccumulators being able to sequester elements from low concentrations in soils, but when the levels in the soils increase, the amount sequestered to the plant does not vary as greatly, making these species unsuitable for exploration purposes as they have consistently high values everywhere (Brooks 1998). Hyperaccumulating plants are potentially useful in cleaning contaminated soils (phyto-remediation) or for mining metals (i.e. phyto-mining) (Black 1995; Brooks *et al.* 1995; Anderson *et al.* 1997; Brooks 1998; Veira & Volesky 2000; Radway *et al.* 2001; Incharoensakdi & Kitjaharn 2002; Yong *et al.* 2002; Akhtar *et al.* 2004; Prasad 2005; Dunn 2007). In each of these cases a hyperaccumulator species is required that also has a high biomass (Brooks 1998).

Not all elements can be hyperaccumulated. The most well known elements for hyperaccumulation are Al, Cu, Co, Mg, Ni and Zn (Prasad 2005). Major plant nutrients are naturally in high levels in all plant species, meaning that they are not considered. There are no known hyperaccumulators for Cr and Ti therefore these elements are often used to determine detritial contamination of vegetation samples (Brooks 1998). However, this study has shown that *Triodia spp.* are able to accumulate high levels of Cr, but this is still not classified as hyperaccumulation. Nickel is the most commonly hyperaccumulated element (Brooks 1998), with over 300 hyperaccumulating species identified (Prasad 2005). Some elements can even compete within the plant for hyperaccumulation (Prasad 2005). This is particularly important in serpentine-derived soils where Co, Cr and Ni are in high concentrations and have similar activities (Prasad 2005).

Few Australian species have been shown as hyperaccumulators (Brooks 1998) one of these is the Ni hyperaccumulator *Hybanthus floribundus* (shrub violet), which has been shown to have Ni concentrations up to 1% within the leaves, but the plants were growing in soils that only had a concentration of 0.07% (Brooks *et al.* 1995). This species is recognised as an indicator as well as a hyperaccumulator which is rare (Cole 1973). It has also been shown to contain high levels of Cr near Widgemooltha in Western Australia (Cole 1973).

2.4 Phyto-mining / remediation

Phyto-mining or phyto-remediation is where hyperaccumulating plants are used over a site for the specific extraction of a particular element. The plant matter is then harvested and ashed to produce the element as a product in phyto-mining, or in phyto-remediation the element is removed from a site (particularly anthropogenic contaminants). In both cases plants are grown to specifically accumulate a particular element, which is then ashed to concentrate the ore or contaminant into a small volume (Anderson *et al.* 1997). For example this can include the extraction of Au where water hyacinth can extract Au from mine tailings (Brooks 1998).

The productivity of phyto-mining or phyto-remediation can be enhanced by treating the soil with enzymes or other compounds while the plants grow. For example, the addition of citric acid can significantly increase plant uptake of Ni (Brooks 1998) or ammonium thiocyanate can be added to soils to aid plants in hyperaccumulating Au (Anderson *et al.* 1997). This also can affect the bioavailability of the element within the soil, which is a crucial factor influencing the elemental uptake by roots (Kamnev & van der Lelie 2000). One of the mechanisms for this is that root exudates can enhance degradative micro-organisms in the soil (which produce organic acids), which in turn stimulates plant growth through increasing the solubility and bioavailability of elements (Kamnev & van der Lelie 2000).

Phyto-remediation is also much cheaper than other forms of soil reclamation. It has been estimated that 'phyto' processes could potentially cost $\$US105/m^3$ as opposed to soil washing, which costs around $\$327/m^3$ (all values are expressed as 1998 dollars as they are estimate costs since no large scale phyto-remediation project has been implemented yet) (Black 1995; Brooks 1998). This process is still in the early stages and to become economical the energy produced by the combustion of the plant material must be harnessed (Brooks 1998). Future work in this field could include genetically modifying plant species to be hyperaccumulators or to selectively breed species with higher biomasses (Brooks 1998).

2.5 Phyto-exploration

Phyto-exploration is the term for using plants specifically in the detection of mineral deposits. Generally spatial plots of elemental concentration are generated, which can highlight geochemical footprints of mineralisation. Lintern *et al.* (1997) indicated that the Au concentrations in some plants could give an indication of depth to mineralisation. However, if there is a geochemical anomaly at the surface, the same response would be generated by a large deposit at depth or a small deposit close to the surface. The width and magnitude of a biogeochemical anomaly is dependant on the primary dispersion from the ore, secondary dispersion at a later time under different environmental conditions, and present day dispersion (Nicolls *et al.* 1965a; Cole *et al.* 1968; Cohen *et al.* 1999). The mobility of the element is very important since low mobility elements (like Pb) will have a smaller geochemical footprint than the highly mobile elements (like Zn) (Cole *et al.* 1968; Cole & Smith 1984).

Lintern *et al.* (1997) even indicated the different possibilities by showing that *Maireana* leaves were effective at mapping out Au mineralisation at the Zuleika site but these results could have been generated by floodplain deposition in that area. The implications of this are that surficial features must be understood before trying to interpret geochemical anomalism.

The use of plants as a sampling medium can have several purposes in mineral exploration. There are 'penetrator' plants, which have deep roots that give a point source geochemical signal and there are 'amalgamator' plants which have broad root systems that provide a geochemical signal from 100s to 1000s of square metres (Hill 2004). Amalgamator plants are

ideal for regional-scale sampling programs (commonly only stream sampling carried out), where samples are collected every 1-10 km, with the target being broad geochemical haloes (Cohen *et al.* 1999; Hill & Hill 2003; Hill 2004). Penetrator plants are ideal for prospect-scale sampling programs, where a broad anomaly has been identified and samples collected every 25-500 m, with the target being ore delineation (Hill & Hill 2003; Hill 2004). Prospect-scale sampling programs are particularly sensitive to landscape changes, as plants growing in a drainage systems will provide a distinct signal from those growing directly into bedrock (Hill 2004).

2.6 Botanical Information for Biogeochemistry Context

Some of the more important botanical information for biogeochemical exploration relates to plant roots. The size and widths of the rooting systems of most Australian species are still not known. The most common types of roots are tap roots, sinker roots and obliquely descending lateral roots, which can all reach great depths (Canadell *et al.* 1996). However, lateral root spread influences how many plants compete for nutrients, so the distance between each plant of a species can give a rough indication of root lengths (Schenk & Jackson 2002). Deep rooting systems require more energy to construct than shallow systems, and shallow soils are often not oxygen deficient whereas deep soils can be (Schenk & Jackson 2002). Typically the older and larger a plant, the wider and deeper the root system (Schenk & Jackson 2002).

Lateral systems are expected to be greatest in arid environments to ensure maximum usage of small rainfall events (Schenk & Jackson 2002), this can often be misleading where there are not many small events but very infrequent large events. In areas where the rainfall is very restrictive, some plants stay dormant in the soil as seeds, and others send roots very deep within the soil to reach a permanent water source, which may be over 18 m below the surface (Canadell *et al.* 1996). As the top layers of the soil are slowly dried out from plants extracting the water, plant roots must go deeper to find water (Canadell *et al.* 1996). Some factors can limit the maximum depth reached by a plant species including: soil bulk density; shallow bedrock; permafrost; the water table saturating the roots; and, horizontal layers of clay or shale that are impermeable (Canadell *et al.* 1996). Plants can sometimes penetrate bedrock or clays through cracks or fissures (Canadell *et al.* 1996). One of the only Australian species recorded was *Eucalyptus marginata,* which had a maximum rooting depth of 40 m (Canadell *et al.* 1996). Other studies have only focussed on tracking roots to the depths of interest to their study for example *Corymbia chippendalei* was found to penetrate to 8 m in a sand dune (Grigg *et al.* 2008a) but this was only the maximum depth excavated to, not the maximum depth of roots. Also *Triodia spp.* were excavated to 3 m depth to determine that they were deep rooting but the maximum depth was never determined (Burbidge 1953; Grigg *et al.* 2008b).

There is little difference between the rooting structures of perennial grasses and small shrubs (Schenk & Jackson 2002). Grasses typically have fibrous root systems and shrubs tend to be tap-rooted, but the magnitude and dimensions tend to be similar (Schenk & Jackson 2002). Most herbaceous plants tend to be active to a depth of 2 m in most arid environments and to 4 m in tropical environments (Schenk & Jackson 2002). The maximum reported rooting depth for a grass is 6 m in *Achnatherum splendens* from the deserts of Kazakhstan (Schenk & Jackson 2002), however, spinifex roots have been seen at depths greater than this in mine pits in the Tanami Desert (Reid *et al.* 2008). DNA testing is now required to further verify this. Maximum rooting depths recorded from selected species across the world ranged from 0.3 m for some tundra species to 68 m for *Boscia albitrunca* in the central Kalahari (Canadell *et al.* 1996).

2.7 *Triodia spp*. detailed background

Since much of the study focussed on the chemical and physical properties shown by the spinifex species (*Triodia spp.*), it was necessary to present a detailed background on what was known about the genus. This genus has potential in becoming a useful sampling medium over large areas of the Australian continent.

Spinifex hummock grasslands are widespread across arid and semi-arid Australia where they occupy at least 22% of the continent (Taylor 1937; Beard 1967; Griffin 1990; Rice & Westoby 1999) (See Figure 2.1). The group is represented in all mainland states and absent only from cold-temperate south-eastern Australia (Lazarides 1997). This makes spinifex grasslands one of the continent's most dominant vegetation types. Hummock grasslands are unique to Australia, but there are similar adaptations to aridity within *Cactaceae* in the Americas and in the *Aizoaceae* and *Liliaceae* in southern Africa (Beard 1967; Rice *et al.* 1994). Research in this field may lead to advances in other countries, e.g. mineral exploration in the prairie of North America and the use of arid grass species in African savannahs. They predominantly grow in areas with well drained, low nutrient soils (Winkworth 1967; Rice *et al.* 1994). *Triodia spp.* are able to tolerate many different soil types and conditions but they tend to be out-competed by other species, hence they are most prevalent in areas where other plant species struggle. They are prevalent on sandplains, dunefields, mountain ranges and hills in arid, semi-arid and seasonally arid (monsoonal) regions of Australia (Beard 1969; Griffin 1990; Lazarides 1997). The greatest diversity of species occurs on mountain ranges and hills in shallow or skeletal soils derived mostly from sandstone, quartzite, limestone and ferruginous materials, but also from granite, shales, slates, basalt and other rocks (Lazarides 1997). In general however, the different spinifex species do no grow together, making local species identification easier (Griffin 1990).

Figure 2.1: Distribution of all spinifex species across Australia, adapted from AUSLIG 1990.

Areas of spinifex grasslands extend across some of Australia's most prospective regions for mineral exploration (e.g. Tanami, Pilbara, Western Kimberley, Mt Isa, Arunta, NE Yilgarn, and Musgraves) and most particularly across some of the most regolith-dominated parts of these regions. Spinifex is also a component of mallee communities in the Gawler Province and in some parts of the Curnamona Province. Many species have very wide distributions; *Triodia scariosa* occurs in all mainland States; *T. basedowii* in all except Victoria; *T. longiceps, T. pungens* and *T. schinzii* in all except New South Wales and Victoria (Lazarides 1997).

The 64 described spinifex species (*Triodia* and *Plectrachne* first categorised by Robert Brown 1810) are perennial, drought-resistant hummock grasses (Burbidge 1946a; Perry 1962; Rice & Westoby 1999). *Triodia spp.* are characterised by their unique drought adaptive (xerophytic) leaf anatomy (Lazarides 1997), where they have tough, pointed, sclerophyllous, and longitudinally folded leaves (Burbidge 1944a; Burbidge 1945; Burbidge 1946a; Burbidge 1953; Perry 1962; Beard 1967; Craig & Goodchild 1977; Lazarides 1997; Rice & Westoby 1999). They are long-lived (10s to 100s of years) and typically form rings due to the senescence of the older centre of the tussock with increasing age (Cochrane 1963; Beard 1967; Beard 1969; Weidemann 1971; Lazarides 1997). In a *Triodia*-dominated region the plants tend to occupy a third of the soil surface with the rest remaining as bare soil (Winkworth 1967). The ground surface in this environment becomes 'hummocky' due to soil and dust build up around the plants, these hummocks allow greater water penetration than between the hummocks (Winkworth 1967; Weidemann 1971).

The degree of drought tolerance that spinifex grasses endure in a vegetative state can be illustrated by *Triodia basedowii* leaves withstanding a diffusion pressure deficit equivalent to about 130 atmospheres of pressure (Perry 1962; Winkworth 1967). This enables the plants to survive all but the most severe, prolonged droughts because their anatomy reduces transpiration from their leaves and by absorbing maximum moisture from soil participles by their ability to apply very high osmotic pressures (Lazarides 1997). Also, *Triodia* plants are deep rooting, highly competitive, and slow-growing (Burbidge 1945; Johnson & Putwain 1981; Lazarides 1997; Churchill 2001). At least one of the species (*Triodia flava*) is tolerant of As (from herbicides) which has strong mineral exploration potential as As is sometimes associated with Au (Malone 1972).

Spinifex are part of the *Danthonieae* group of grasses and have some similarities to other genus within the group (de Wet 1956). They are all within the C4 group of plants (McWilliam & Mison 1974; Craig & Goodchild 1977; Wooller *et al.* 2005). *Triodia spp.* contain long siliceous rich cells which are similar to those seen in *Danthonia spp.* (de Wet 1956). These cells in spinifex are very rich in silica, which gives them rigid structure. One of the differences between spinifex and other grasses in the group is that the bundle sheath cells of spinifex connect to other bundle sheath cells rather than the epidermis (surface) cells, which allows increased rigidity (McWilliam & Mison 1974; Brown 1975). Their anatomy is such that they can tolerate low nutrients, high light and high temperatures (McWilliam & Mison 1974; Craig & Goodchild 1977).

Triodia spp. are extremely flammable, some species produce resin (e.g. *Triodia pungens*), which increases this flammability (Rice & Westoby 1999). This method makes them similar in many ways to sclerophyllous forests, where the oils of *Eucalyptus spp.* make them extremely flammable (Rice & Westoby 1999). Spinifex have 2 methods of surviving fire events, there are resprouting species (growing from a root stock) and seeding species (growing from seed in the soil) (Burbidge 1944a; Rice & Westoby 1999). This has implications for their potential to take up nutrients and their rooting depths. Resprouting species would live longer and hence grow deeper roots than seeding species. Resprouting

species are more common in areas where fires are frequent (e.g. Tanami) (Casson & Fox 1987; Rice & Westoby 1999).

3 Methodology

The search for new mineral resources is hampered by transported cover and the lack of low-cost, developed methods which can be applied by exploration companies. Biogeochemistry is one method that has been applied in many terrains and climates which can be used to identify mineralisation signatures. There is a need to refine this process to sampling several species over small-scale surveys which can be presented as an applied form to mineral explorers. Within Australia there have been few plant species that have been investigated for this purpose and there has been little progress into adapting this methodology into quick orientation programs which exploration companies can use to survey their tenements. This study focussed on taking samples of several species from several sites rather than one species from one site in order to see if small-scale sampling strategies could be used effectively for mineral exploration. Sampling many species also helps to determine whether any plants have specific properties which may be of use in other fields besides mineral exploration, and to find the optimum species to be sampled in these terrains.

3.1 Geobotanical methods

Species names and associated understorey species were recorded at each site where a biogeochemical sample was taken. This was used to make observations about landscape controls on species distributions. At the Coyote Prospect, each tree, shrub and grass was recorded along all transects sampled. At each tree or large shrub, the height and species name was recorded as well as the understorey species.

3.2 Biogeochemical methods

3.2.1 Sample collection

Each sample was collected while wearing powder-free, latex gloves or in the case of spinifex nitrile gloves. The gloves were changed between samples to prevent chemical build-up on the surface of the glove and contamination between samples (Figure 3.1).

Figure 3.1: Samples being collected at the Coyote Prospect.

Plants in good health were chosen and immature plants and those growing in or near drill spoil were avoided. Samples were collected over the dry season as this has previously been shown to have generated the highest anomalism (background to elevated values ratio) in other areas (Cruickshank & Pyke 1986; Stanton 1988; Brooks 1998; Hulme & Hill 2004). Leaves / phyllodes were chosen as the target plant organ because they have given the best results in previous studies (Hall *et al.* 1973; Davy & Ryall 1980; Lintern *et al.* 1997; Cohen *et al.* 1999; Hulme & Hill 2003). Samples had minimal disease and infestation, minimal surface dust contamination, were middle aged (i.e. not juvenile or senescent), were readily available, and had a healthy appearance. Samples were placed in brown paper bags, allowing the samples to breathe and reduce sample degradation, and were folded over at the top. Most spinifex samples were 'double bagged' as to reduce the likelihood of the sample piercing the bag and gaining contaminants.

3.2.2 Sample preparation and analysis

The vegetation samples were then dried in a low temperature oven (45^{o} C for 48 hours). The samples were not washed as previous work by Karen Hulme had shown that washing provided negligible removal of dust contaminant particles (K. Hulme, pers. comm 2005; Dunn, 2007; Anand, 2007) These dried samples were ground to a fine powder using a rotating blade, stainless steel mill. Assays for the Coyote, Larranganni and Hyperion Prospects were done by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and Optical Emission Spectrometry (ICP-OES) through Genalysis Laboratories, Western Australia, where the samples were subjected to a cold, concentrated nitric acid digest overnight, then a concentrated perchloric acid digest to break up the organic component, then the fully digested sample was run through the ICP mass spectrometer and ICP optical emission spectrometer. The elements analysed were: ICP-MS: Ba, Be, Bi, Cd, Co, Ga, In, Mo, Nb, Nd, Pb, Sn, and Sr, ICP-OES: Al, Cu, Mg, Mn, Ni, P, S, Ti, V and Zn. Additional elements analysed for Hyperion were: B, Ca, Ce, Cr, Cs, Dy, Er, Eu, Fe, Gd, Hf, Ho, K, La, Li, Lu, Na, Pr, Rb, Re, Se, Sm, Ta, Tb, Th, Tl, Tm, U, Y, Yb and Zr. Instrumental Neutron Activation (INAA)

analysis for these samples was performed by Becquerel Laboratories, Canada, where 8 g of sample is compressed into a briquette, shrink-wrapped then irradiated with a neutron source; the gamma rays emitted from the sample are measured for the element type and concentration present. The elements Analysed were: Ag, Au, As, Ba, Br, Cd, Ca, Ce, Cs, Cr, Co, Eu, Hf, Ir, K, Fe, La, Lu, Mo, Ni, Rb, Sb, Sc, Se, Sm, Na, Ta, Te, Th, W, U, Yb, Zn and Zr. Assays for the Titania, Pine Creek and Tunkillia samples were done by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), which was performed at ACME Laboratories, Canada, where the samples were subjected to a nitric acid and modified Aqua Regia digest then run through a Perkin Elmer Elan 6000 ICP-mass spectrometer. The elements analysed were: Au, Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ge, Ga, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, and Zr.

3.2.3 Soil sampling

Surface soil samples were collected from the Coyote and Titania Prospects, corresponding to sites where vegetation samples were collected. The samples were originally collected with the aim of analysing the microbial component of the soils. This aspect was stopped due to lack of time and funding, but the samples were still deemed useful as a comparison between the vegetation chemistry, and the drill logs. Thus far only the Titania samples have been assayed due to financial constraints.

Since the soil samples were collected with microbial properties in mind, they were sampled in a different way from 'normal' soil geochemical samples. Each soil sample was collected from the very top surface where cryptogam density was greatest. Microbes are well known for accumulating metals and in particular Au (Reith *et al.* 2006). Each sample was collected while wearing powder-free, latex gloves or in the case of spinifex nitrile gloves. The gloves were changed between samples to prevent chemical build-up on the surface of the glove and contamination between samples. The top 5 cm of soil was collected within a 30 cm by 30 cm square with a plastic shovel and placed into plastic 'zip-seal' bags.

If the sample was wet, it was placed into a low temperature oven and dried at 45^{o}C for 48 hours. The sample was then sieved to less than 75μm fraction using a nylon mesh and plastic sieve. The samples were not crushed or macerated due to them being mostly sands and silt particles with very little cohesion.

The fine fraction was then shaken to homogenise and then split with one 5 g amount being sent to ACME Laboratories, Canada, for ICP-MS analysis. Where the samples were subjected to a nitric acid and modified Aqua Regia digest then run through a Perkin Elmer Elan 6000 ICP-mass spectrometer. The elements analysed were: Au, Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ge, Ga, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, and Zr. Three samples of the standard reference material, OREAS 42P, was included with the batch to help provide QA/QC as well as sample duplicates.

3.2.4 Quality assurance / quality control

Contamination risk was reduced for sampling by removing all watches, jewellery and other metallic objects. Hands were kept clear of sunscreen by washing and drying, and wearing a hat and sensible clothing rather than needing sunscreen.

The validity of the analytical procedures was calculated by laboratory duplicate samples taken from every 30th sample, of the full data set. The split of the sample was performed by grinding the entire sample to powder form, then shaking, rotating and agitating the sample to ensure homogeneity, then half the sample was placed into a new bag as a duplicate. Field sampling error was reduced by using the rigorous methodology adapted from (Hill 2002; Hulme & Hill 2003). Laboratory standard reference materials (V14 – mountain hemlock needles, Figure 3.2) and blanks were used to provide an assessment of the analytical bias of the concentrations; these results were incorporated into the error values presented in Appendix B, all errors were similar or lower than those predicted by the standard errors from Figure 3.2.

CERTIFICATE OF ANALYSIS

V14

Internal Reference Material for 1VE Vegetation Digestion

ELEMENT	Unit	Group 1VE Detection Limit	Expected Value	Standard Deviation*
Au	ppb	0.2	8.6	7.0
Ag	ppb	2	24	3
Al	%	0.01	0.15	0.01
As	ppm	0.1	11.3	2.9
B	ppm	1	17	1
Ba	ppm	0.1	1.4	0.1
Bi	ppm	0.02	0.09	0.01
Ca	%	0.01	0.67	0.03
Cd	ppm	0.01	0.23	0.01
Co	ppm	0.01	0.83	0.05
Cr	ppm	0.1	1.2	0.2
Cu	ppm	0.01	5.17	0.21
Fe	%	0.001	0.016	0.001
Ga	ppm	0.1	0.1	0.0
Hg	ppb	1	52	4
K	%	0.01	0.51	0.03
La	ppm	0.01	0.03	0.01
Mg	%	0.001	0.079	0.004
Mn	ppm	1	2145	105
Mo	ppm	0.01	0.07	0.05
Na	%	0.001	0.002	0.001
Ni	ppm	0.1	1.5	0.2
P	%	0.001	0.093	0.008
Pb	ppm	0.01	0.88	0.07
S	%	0.01	0.06	0.02
Sb	ppm	0.02	0.07	0.01
Sc	ppm	0.1	0.1	0.0
Se	ppm	0.1	0.2	0.1
Sr	ppm	0.5	6.7	0.4
Te	ppm	0.02	<0.02	
Th	ppm	0.01	<0.01	
Ti	ppm	1	7	1
Tl	ppm	0.02	0.04	0.01
U	ppm	0.01	<0.01	
V	ppm	2	<2	
W	ppm	0.1	<0.1	
Zn	ppm	0.1	15.8	1.0

ELEMENT	Unit	Detection Limit	Expected Value	Standard Deviation*
Optional Elements				
Cs	ppm	0.005	0.029	0.001

Figure 3.2: Error analysis for the V14 standard reference material (Acme Laboratories and Dr. Colin Dunn 2006).

3.2.5 Data analysis

Elemental concentration was plotted as a layer over the geo-rectified aerial photograph in ArcGIS 9.0 to show the location of assays with respect to the surface projection of known

mineralisation extents and landscape features. The cut-offs for each concentration range were using the natural breaks function in ArcGIS which matched up with values determined from tukey-plots produced in the program IoGas, which gave quantitative numbers for extreme outliers, outliers, upper and lower hinges of the box and the top and lower bounds of the box. Species differences were plotted as probability plots within IoGas with the different species represented by different symbols.

3.3 Organ differentiation

Previous investigation of the literature indicated that leaves would be the most appropriate plant organ to sample in Australian environments. However, it was thought that proof of this theory would be beneficial in understanding the processes involved in elemental uptake, storage and contamination effects. Leaves, seed stalks and roots were examined of spinifex species, there was no leaf litter at most sites due to either fire or wind. Leaves, twigs, bark, buds and leaf litter were collected from several *Eucalyptus/Corymbia* species as well as from a dogwood at the Coyote Prospect.

Stalks and leaves of 3 *Triodia irritans* plants were collected at the Maralinga sites near local water holes. The chemical differences can be seen in Appendix C, where in almost all elements the leaves contained the highest concentrations. The exceptions were Al, As, Ce, Cs, Fe, Hf, Hg, La, Na, Nd, Pb, Pr, Sb, Sn, Th, Ti, Y and Zr. Interestingly, Al, Fe, Hf, Th, Ti and Zr are considered to be potential contaminant elements, which indicates that in this environment the stalks (which grow above the main plant body) can collect greater amounts of contamination from wind blown dust. Therefore leaves are the best sampling medium for this species. In general the potential for an organ to collect wind-blown dust is dependant on the surface of the organ. Most plant species in arid environments have smooth, waxy leaf surfaces which resist dust build-up.

Stalks, leaves and the roots of 2 *Triodia pungens* plants were collected at the Titania and Hyperion Prospects. The chemical differences can be seen in Appendix C, where the leaves were highest in B, Ba, Ca, Cr, Fe, K, Mg, Mn, Na, Ni, P, S, Se, Sr, Ta and Ti, the stalks were highest in Al, As, Ce, Hf, Hg, La, Pb, Pr, Sn, Y and Zr, the roots were highest in Au, Cd, Co, Mo, Th and Zn. Several elements were not considered not significantly different (Cs, Cu, Ge, Li, Rb, Sb, Sc and Sm) these elements were of comparable levels in all plant organs.

Leaves, leaf litter, buds and twigs of 5 *Eucalyptus brevifolia* plants were collected at the Coyote Prospect at 500 m spacings. The chemical differences can be seen in Appendix C, where the leaves had the highest levels of Ba (northern samples), Br, Ca, P and S, the litter was highest (with twigs being close but slightly less) in Al, As, Au, Ba (southern samples), Ce, Co, Cr, Fe, La, Mn, Nd, Ni, Sc, Sm, Sr, Th and Zn, the buds were highest in K and Rb. The elements that were not significantly different were Cu, Mg, Mo and Sn.

3.4 Field site sampling summary

Table 1: Summary of field sampling dates and species sampled at each site.

Field Site	Sampling Date	Target Species
Coyote	19 – 27 Feb 2005 18 Jan – 4 Feb 2006	*Triodia pungens,* *Eucalyptus brevifolia,* *Eucalyptus pruinosa* *Corymbia opaca,* *Acacia coriacea subsp. sericophylla.*
Larranganni	25 February 2005	*Eucalyptus brevifolia.*
Titania	4 – 14 Oct 2005 15 – 25 Aug 2006	*Triodia pungens,* *Melaleuca lasiandra,* *Melaleuca glomerata,* *Acacia bivenosa,* *Acacia coriacea subsp. sericophylla,* *Hakea macrocarpa,* *Grevillea striata,* *Eucalyptus pachyphylla,* *Corymbia opaca.*
Hyperion	9 Oct 2005	*Triodia pungens,* *Eucalyptus brevifolia,* *Eucalyptus pruinosa,* *Acacia coriacea subsp. sericophylla,* *Acacia lysiphloia.*
Johns Hill	21 Nov 2006	*Heteropogon triticeus,* *Melaleuca virirflora,* *Corymbia polycarpa.*
Great Northern	22 Nov 2006	*Heteropogon triticeus,* *Melaleuca virirflora,* *Eucalyptus foelscheana.*
McKinlay	23 Nov 2006	*Heteropogon triticeus,* *Corymbia polycarpa,* *Eucalyptus foelscheana ,* *Eucalyptus miniata.*
Glencoe	24 Nov 2006	*Heteropogon triticeus,* *Eucalyptus miniata.*
Tunkillia	12-13 Feb 2007	*Triodia irritans.*

4 Tanami Region – Background

4.1 Introduction

The Tanami Desert of northern Australia is highly prospective for mineral exploration, due to the number of known mineral deposits in the area and the large areas that have been under-explored. The first crossing of the Tanami Desert was by Nat Buchanan in 1896 (Gibson 1986). When gold was discovered in 1904 mineral exploration soon boomed in the region (Gibson 1986; Tunks & Crooke 2007). Several large deposits have been developed since Au was discovered in the 1900s (Wilford 2000). It hosts the world-class Callie Au-deposit (Cross *et al.* 2005) and other smaller deposits and prospects. However, most of these deposits were found in outcrop, or immediately around outcrop as undercover extensions (Perry 1962). Outcrop across the region is sparse, which means large areas of the Tanami are under-explored (Wygralak *et al.* 2001; Crispe *et al.* 2007). The transported cover materials are mostly between 10-20 m thick with some palaeo-drainage systems reaching a thickness of over 100 m (Wilford 2003). Pattern drilling of surface geochemical or geophysical targets has been widely used in this area but is extremely expensive, time consuming, and has been of limited success (Gibbons & Webb 1997; Wilford 2000; Wilford 2003; Petts & Hill 2005; Worrall *et al.* 2007; Reid *et al.* 2008). The high prospectivity but lack of exploration success associated with the covered areas demands that other mineral exploration techniques be developed, with the objective of providing a surficial chemical expression of mineralisation buried by transported regolith that contains either geochemically barren or complexly dispersed geochemical expressions of underlying mineralisation.

4.2 Location and Geology

The Tanami Desert occupies roughly 160,000 km^2 covering the central west of the Northern Territory and into Western Australia (Gibson 1986). The northern, eastern and south-eastern parts are comprised of pastoral leases for cattle grazing and the rest is mostly Aboriginal Reserve (Gibson 1986). Due to the large amount of Aboriginal Reserve access to the Tanami region is restricted to the Tanami Highway (Gibson 1986).

The region hosts a number of significant Au deposits in addition to the deposits examined in this study (Figure 4.1) (Huston *et al.* 2007; Mernagh & Wygralak 2007; Tunks & Crooke 2007). The largest deposit is Callie, which is characterised by sheeted vein sets in the hinges of folded carbonaceous rocks within the Dead Bullock Formation, which is overlain by the Killi Killi Formation turbidites (Cross *et al.* 2005; Adams *et al.* 2007; Bagas *et al.* 2007; Crispe *et al.* 2007; Williams 2007). The Killi Killi Formation (1840 – 1830 Ma) is comprised of siltstones and sandstones and is the youngest member of the Tanami Group (Crispe *et al.* 2007). The basal unit of this group is the Dead Bullock Formation, a fining-upward deep water succession dominated by siltstone, carbonaceous siltstone, iron formation and mafic sills. The Tanami Group is underlain by Archaean (2550-2500 Ma) rocks and is overlain by rhyolite, ignimbrite, siliciclastic sediment and felsic ignimbrite of the Ware Group (1825-1810 Ma). Rocks of the Tanami and Ware Groups were intruded by granites (1825 -1790 Ma) which have been subdivided on geochemical criteria into the Birthday, Frederick and Grimwade Suites. In the Tanami Mine corridor the Ware Group is overlain by basalt and immature sediment of the Mount Charles Formation, which are interpreted to reflect a continental rift succession (Huston *et al.* 2007). The age of this succession is poorly constrained, but it is likely to have been deposited at about 1800Ma, with an early Archaean sedimentary provenance distinct from that of the Tanami and Ware Groups.