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GOLD AND ASSOCIATED ELEMENTS IN THE REGOLITH - DISPERSION PROCESSES AND IMPLICATIONS FOR EXPLORATION

P241 Final Report

*C.R.M. Butt, D.J. Gray, M.J. Lintern
I.D.M. Robertson, G.F. Taylor and K.M. Scott*

CRC LEME OPEN FILE REPORT 29

November 1998

(CSIRO Division of Exploration Geoscience Report 167R, September 1991.
Second impression 1998)

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RESEARCH ARISING FROM CSIRO/AMIRA REGOLITH GEOCHEMISTRY PROJECTS 1987-1993

In 1987, CSIRO commenced a series of multi-client research projects in regolith geology and geochemistry which were sponsored by companies in the Australian mining industry, through the Australian Mineral Industries Research Association Limited (AMIRA). The initial research program, "Exploration for concealed gold deposits, Yilgarn Block, Western Australia" (1987-1993) had the aim of developing improved geological, geochemical and geophysical methods for mineral exploration that would facilitate the location of blind, buried or deeply weathered gold deposits. The program included the following projects:

P240: Laterite geochemistry for detecting concealed mineral deposits (1987-1991). Leader: Dr R.E. Smith.

Its scope was development of methods for sampling and interpretation of multi-element laterite geochemistry data and application of multi-element techniques to gold and polymetallic mineral exploration in weathered terrain. The project emphasised viewing laterite geochemical dispersion patterns in their regolith-landform context at local and district scales. It was supported by 30 companies.

P241: Gold and associated elements in the regolith - dispersion processes and implications for exploration (1987-1991). Leader: Dr C.R.M. Butt.

The project investigated the distribution of ore and indicator elements in the regolith. It included studies of the mineralogical and geochemical characteristics of weathered ore deposits and wall rocks, and the chemical controls on element dispersion and concentration during regolith evolution. This was to increase the effectiveness of geochemical exploration in weathered terrain through improved understanding of weathering processes. It was supported by 26 companies.

These projects represented "an opportunity for the mineral industry to participate in a multi-disciplinary program of geoscience research aimed at developing new geological, geochemical and geophysical methods for exploration in deeply weathered Archaean terrains". This initiative recognised the unique opportunities, created by exploration and open-cut mining, to conduct detailed studies of the weathered zone, with particular emphasis on the near-surface expression of gold mineralisation. The skills of existing and specially recruited research staff from the Floreat Park and North Ryde laboratories (of the then Divisions of Minerals and Geochemistry, and Mineral Physics and Mineralogy, subsequently Exploration Geoscience and later Exploration and Mining) were integrated to form a task force with expertise in geology, mineralogy, geochemistry and geophysics. Several staff participated in more than one project. Following completion of the original projects, two continuation projects were developed.

P240A: Geochemical exploration in complex lateritic environments of the Yilgarn Craton, Western Australia (1991-1993). Leaders: Drs R.E. Smith and R.R. Anand.

The approach of viewing geochemical dispersion within a well-controlled and well-understood regolith-landform and bedrock framework at detailed and district scales continued. In this extension, focus was particularly on areas of transported cover and on more complex lateritic environments typified by the Kalgoorlie regional study. This was supported by 17 companies.

P241A: Gold and associated elements in the regolith - dispersion processes and implications for exploration. Leader: Dr C.R.M. Butt.

The significance of gold mobilisation under present-day conditions, particularly the important relationship with pedogenic carbonate, was investigated further. In addition, attention was focussed on the recognition of primary lithologies from their weathered equivalents. This project was supported by 14 companies.

Although the confidentiality periods of the research reports have expired, the last in December 1994, they have not been made public until now. Publishing the reports through the CRC LEME Report Series is seen as an appropriate means of doing this. By making available the results of the research and the authors' interpretations, it is hoped that the reports will provide source data for future research and be useful for teaching. CRC LEME acknowledges the Australian Mineral Industries Research Association and CSIRO Division of Exploration and Mining for authorisation to publish these reports. It is intended that publication of the reports will be a substantial additional factor in transferring technology to aid the Australian Mineral Industry.

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Sampling the deep saprolite: a stimulating aspect of regolith research.

FOREWORD

INTRODUCTION

The CSIRO - AMIRA project "Exploration for Concealed Gold Deposits, Yilgarn Block, Western Australia" had the overall aim of developing improved geological, geochemical and geophysical methods for mineral exploration to facilitate the location of blind, concealed or deeply weathered gold deposits. The project had three partly overlapping research modules, with each module funded separately, although with many sponsoring companies in common.

The research summarized in this report formed Module 2 of this project and was entitled "Gold and associated elements in the regolith - dispersion processes and implications for explorations." (AMIRA Project P241)¹. This Module aimed, in part, to take advantage of the unprecedented opportunities presented by the many open cut gold mines to document and study the deep regolith and the distribution of gold and other elements within it. In addition, detailed field and laboratory studies were conducted to investigate the processes of rock weathering and, specifically, the mechanisms by which gold has been dispersed during the evolution of the regolith on the Yilgarn Block. The results of the research are summarized, integrated and discussed in this Final Report but, for full details, reference should be made to the Investigation Reports, which are listed in Appendix 1. The Investigation Reports contain all the data generated by the project, many with the data on computer disk. The research has involved staff from the Floreat Park and North Ryde laboratories of the Division of Exploration Geoscience.

SPONSORSHIP

The Project was initially sponsored by 26 mining and exploration companies, although the economic recession and mergers reduced this to 22 by the end of the project (Table 1). The large number of sponsors had the advantage of providing access to a wide range of possible research sites and of reducing the "risk" to any individual company in support of strategic research. A disadvantage was that it became very difficult for the research group to develop adequate rapport with geologists and geochemists from sponsoring companies not directly involved in particular investigations and to transfer the results of the research effectively. These problems were partly overcome by initiating a series of informal meetings with staff from each company, to replace some formal presentations.

Table 1. Sponsors of AMIRA Project 241

Aberfoyle Resources Ltd.	F. Lubbock and Associates Pty. Ltd.
Aztec Mining Company Ltd.	Metana Minerals N.L. Pty. Ltd.
Barrack Mine Management Pty. Ltd.	Minsaco Resources Pty. Ltd.
BHP-UTAH Minerals International	Miralga Mining N.L.
Billiton Australia.	Newmont Australia Ltd.
CRA Exploration Pty. Ltd.	Normandy-Poseidon Ltd.
Croesus Mining Ltd.	Pancontinental Mining Ltd.
Dominion Mining Ltd.	Placer Pacific Pty. Ltd.
Geochemex Australia.	Renison Goldfields Consolidated Ltd.
Geopeko.	RTZ Ltd.
Homestake Australia Ltd.	Western Mining Corporation Ltd.

The other modules are:

Module 1. Laterite geochemistry for detecting concealed mineral deposits.
AMIRA Project P240. Project Leader: R.E. Smith

Module 3. Remote sensing for gold exploration in Western Australia.
AMIRA Project P243. Project Leader: A.R. Gabell

OBJECTIVES

The objectives of the project were:

- I. To obtain a better understanding of the nature and genesis of lateritic and supergene gold deposits.
- II. To determine characteristics useful for exploration, especially in areas of transported overburden, for:
 - a. further lateritic and supergene deposits, and
 - b. primary mineralization - including that having no significant overlying secondary mineralization.
- III. To increase knowledge of the properties and genesis of the regolith.
- IV. To provide data applicable to exploration for other commodities in and beneath the regolith.

More specifically, the research had the following aims:

- i. to document the geochemical and mineralogical associations of gold in and close to lateritic and supergene gold mineralization.
- ii. to recommend sampling, sample preparation and analytical procedures for exploration for further secondary and primary mineralization.
- iii. to recommend appropriate pathfinder elements usable in exploration.
- iv. to recommend procedures for data manipulation and interpretation.
- v. to establish criteria for recognizing important units within the regolith, including potentially mineralized horizons.
- vi. to establish criteria for identifying bedrock lithology from its weathered equivalent.
- vii. to develop a system of nomenclature and classification for the deeply weathered regolith.

The research was organized into investigations in five main fields:

1. *Mineralogy and geochemistry of rock weathering.* Mineralogical, petrographic and geochemical studies of the processes of rock weathering were aimed at establishing criteria for rock identification and the recognition of ore environments. Principal sites: Reedy, Panglo, Mt. Magnet (Parkinson pit), Mt. Percy, Beasley Creek, Horseshoe, Bottle Creek.
2. *Gold mineralization and profile development.* The dispersion of gold and associated elements during weathering was studied by determining the morphological, mineralogical and geochemical characteristics of lateritic and supergene gold deposits within the context of profile formation. Principal sites: Mt. Percy, Reedy, Panglo, Callion, Beasley Creek, Bottle Creek, Cork Tree Well, Telfer.
3. *Composition and morphology of gold.* This involved the separation and electron-optical examination of free and particulate gold within the regolith as a guide to its source and conditions of formation. Principal sites: Bardoc, Reedy, Beasley Creek, Mt. Percy, Panglo, Callion.
4. *Gold distribution in the near surface.* The 'residence' and mineralogical association of gold in near-surface horizons of the regolith was determined with particular reference to the role of secondary minerals, organic matter and plants. The research concentrated on determining procedures and criteria for recognizing minor surface enrichments in calcareous horizons. Principal sites: Mt. Hope, Panglo, Mulline, Mt. Percy, Callion, Youanmi, Beasley Creek.

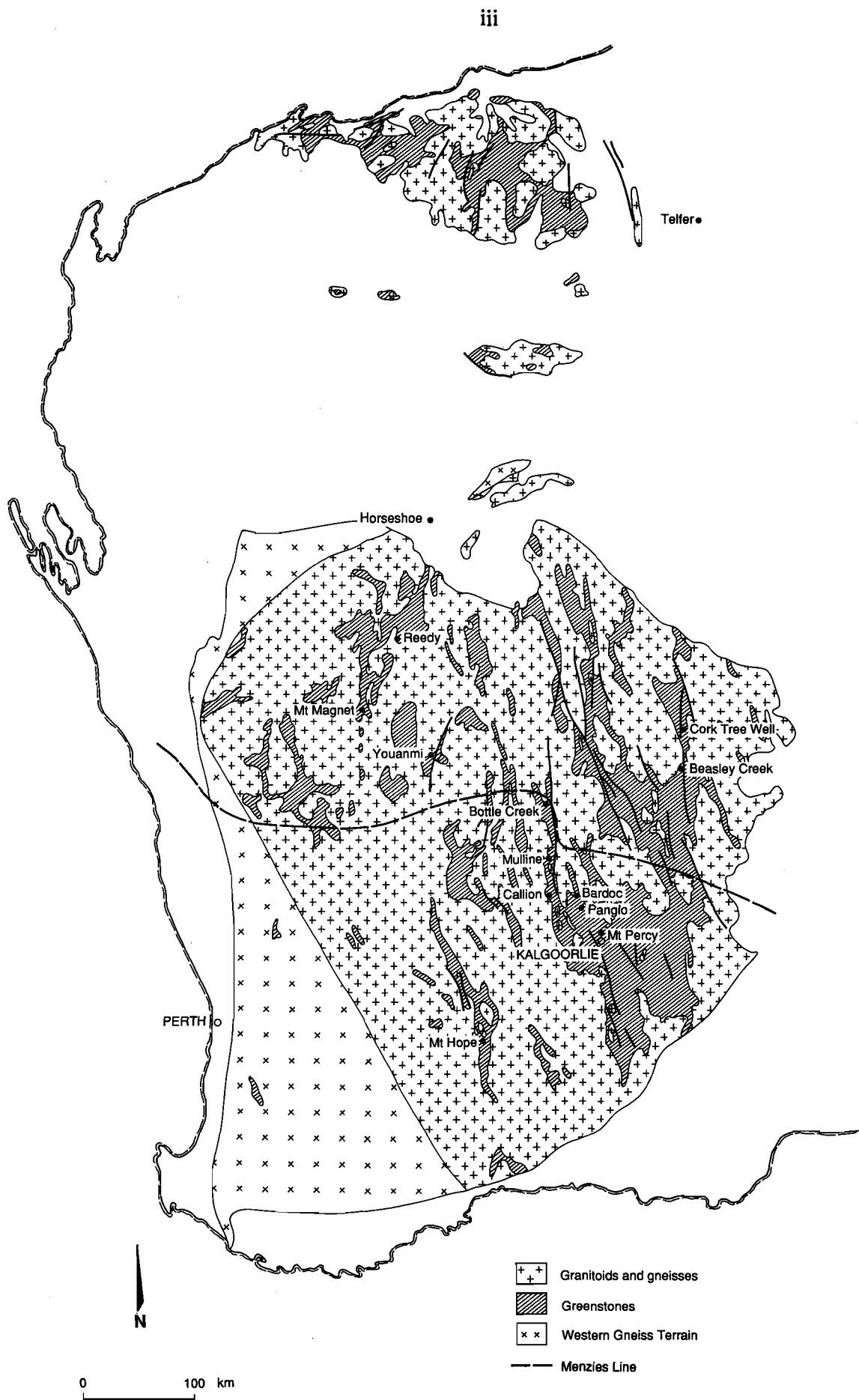


Figure 1. Location of study areas, showing the approximate position of the Menzies Line (after Butt *et al.*, 1978).

5. *Solution chemistry of gold during weathering.* This involved field and laboratory studies of the conditions of gold mobilization and precipitation in the weathering environment. Field site: Panglo. Laboratory studies: chemical interactions of gold with soils, soil minerals and organic matter.

The principal findings in each of these fields are summarized in this report, with reference made to the aims and objectives of the Project as a whole. The locations of the research sites are shown on Figure 1 (p. iii).

PROJECT PERSONNEL

Floreat Park Laboratory.

North Ryde Laboratory

Project Staff:

C.R.M. Butt (Project Leader)
I.D.M. Robertson
D.J. Gray
M.J. Lintern
H.M. Churchward
A.Z. Gedeon
D.L. Longman
R. Bilz

G.F. Taylor
K.M. Scott
J.R. Wilmshurst
S.M. Llorca
R.A. Binns
H. Han

Visiting Scientists:

P. Freyssinet, Strasburg, 1987.
S.F. Gall, Hannover, 1987-8.

M.A. Chaffee, USGS, 1988.

Support Staff:

A.J. Bowyer
G. Burkhalter
J.F. Crabb
M.K.W. Hart
C. Harris
A. Howe
J. Porter
B.W. Robinson
C.R. Steel
A. Vartesi
J.A. Wildman
M.J. Willing

J.J. Davis
L.E. Dotter
J.C. Eames
G.W. Hansen
B.L. Gardner
A. Horne
M.T. Kassis
A. Martinez

C.R.M. BUTT
Project Leader

September, 1991

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SUMMARY

This report summarizes, integrates and discusses the results of over three years of research. The research had the objectives of (a) obtaining a better understanding of the nature and genesis of the regolith and the lateritic and saprolitic gold deposits contained within it, and (b) determining characteristics useful in exploration for further such deposits and for primary mineralization. These rather broad, strategic objectives have been met by some specific lines of research carried out at 16 different sites, mostly in the Yilgarn Block, and have been reported in about 40 Investigation Reports. Some of the highlights of the research include:

1. Data on multi-element dispersion in the regolith at nine mine sites, demonstrating the geochemical expression of gold mineralization.
2. Detailed mineralogical, petrographic and geochemical studies of a range of different lithologies as an aid to bedrock identification from weathered material.
3. Petrographic studies of rock weathering and (in collaboration with AMIRA Project 240), demonstration of the origins of the components of ferruginous lag.
4. A comparison of the morphologies and compositions of gold grains in semi-arid and humid tropical regions, and the implications for gold mobility and the genesis of supergene gold deposits.
5. Demonstration of the significance of soil carbonate horizons as sample media in gold exploration.
6. Demonstration of the existence and characteristics of groundwaters mobilizing gold under present conditions.
7. Further investigations of the chemistry of gold in the weathering environment and demonstration of the high solubility of gold in some soils.
8. Mineralogical and geochemical characteristics of a continuous section through primary gold mineralization (Mt. Percy).
9. Data on the biogeochemical expression of gold mineralization.

1.0 PROJECT OVERVIEW: REGOLITH EVOLUTION AND ELEMENT REDISTRIBUTION

1.1 INTRODUCTION

The data obtained during this Project are consistent with many of the general features established for the evolution of the regolith in semi-arid regions of the Yilgarn Block (Butt, 1981, 1989b; Mabbutt, 1980). In this section, some of the principal findings of the project are summarized and discussed in terms of the impact of the various stages of this evolution on element distributions. More detailed discussions of various aspects of the results are given in other sections of this Final Report, or in specific Investigation Reports.

The regolith of the Yilgarn Block has developed over a very long period, probably since at least the mid-Mesozoic, during which it has been subjected to several major climatic changes. Two climatic regimes have been of particular importance. These were, firstly, humid, warm to tropical periods during the Cretaceous to mid-Miocene and, secondly, drier climates since the Miocene that have continued to the present. The former, which were probably equivalent to climates prevailing in the present wetter savannas, gave rise to extensive, deep lateritic weathering. The later arid to semi-arid climates, and some minor uplift, have resulted in a general lowering of water-tables, changes to, and slowing of, chemical weathering, and erosional modification of the land surface.

Element distributions in the regolith are determined by the stability of their primary host minerals, the chemical mobility of the elements in the weathering environment and the presence or absence of possible secondary host minerals. These in turn are related to the different weathering processes that prevailed during the principal climatic regimes. It is evident that, in general, only the processes that refer to past regimes of long duration, to extreme climates or to recent regimes have had a significant effect. Thus, many of the dominant geochemical (and mineralogical) characteristics of the regolith are related to the development of the lateritic profile under humid climates with high water-tables and generally acid conditions, whereas others are due to later, possibly still active, events related to arid, alkaline environments with lower water-tables. The features produced by these later events appear as modifications of the pre-existing lateritic regolith and tend to be reflected by the concentrations of its minor components.

1.2 LATERITIC WEATHERING UNDER HUMID TROPICAL CONDITIONS

1.2.1 Principal characteristics

1. *Oxidation of sulphide minerals*

At each site, S has been strongly leached from the deepest levels of the regolith and appears to be the element most susceptible to weathering. This observation is consistent with the conclusion that sulphides are some of the most unstable minerals in humid, oxidizing environments, rarely persisting into the weathering zone except as supergene phases such as marcasite, chalcocite and violarite. Nevertheless, relict sulphides (principally pyrite) may persist high in the profile (e.g., at Mt. Percy), preserved within vein quartz.

Many elements hosted by the sulphides (Cd, Co, Cu, Mo, Ni, Zn), the first minerals to weather, are commonly strongly leached deep in the profile. However, these metals are also hosted by other, more stable primary minerals (e.g., Ni, Co in ferromagnesian minerals in ultramafic rocks), which may be the dominant sources in sulphide-poor systems. They are thus retained higher in the profile, but nevertheless are leached from the upper horizons and reprecipitated with secondary minerals such as Fe oxy-hydroxides in the mid to lower saprolite. By analogy with the formation of Ni laterites, some leaching and redistribution of Ni, Co and Mn is probably related to post-lateritic periods of lower water-tables.

2. *Strong leaching of alkali and alkaline earth metals*

Sodium, Ca and Sr are hosted mainly by readily weatherable minerals such as feldspars and carbonates, so that they are reduced to very low concentrations throughout most of the regolith. Potassium, Rb and Cs are also leached if hosted by minerals such as biotite and orthoclase. In many of the research sites, however, they are present mainly in muscovite which becomes appreciably weathered only in the lateritic duricrust, so that concentrations are maintained or residually increased through much of the regolith. Similarly, Mg is strongly leached where hosted by dolomite or amphiboles, but where present in more resistant ferromagnesian minerals (e.g., talc, chlorite), it may be retained through much of the saprolite. Barium, commonly hosted by feldspars, is released early during weathering, but is reprecipitated as barite which remains stable through the regolith and is only partly leached in the duricrust. Enrichments of the alkali and alkaline earth elements high in the profile are commonly due to precipitation under arid conditions.

3. *Retention and concentration of less mobile major elements*

The data obtained during the project illustrate one of the principal characteristics of lateritic regoliths, namely the tendency for their chemical and mineralogical compositions to be dominated by three elements, Si, Al and Fe resident in kaolinite, quartz, iron oxides (hematite and goethite) and, in places, gibbsite. The distributions of several minor and trace elements (e.g., Cr, Sc, Ga, V, As and, possibly, Au) are controlled wholly or in part by the distributions of these major elements. In addition, many resistate and immobile elements also tend to accumulate with Fe oxides in the lateritic horizons although, for most, no chemical interactions are involved.

The abundances and distributions of Si, Al and Fe broadly reflect their source lithologies. Thus, kaolinization of saprolites is strongest over the felsic rocks, and only tends to be well developed over mafic and ultramafic rocks in the upper saprolite. Quartz is only very slightly weathered and most is left as a residual, resistate mineral, most abundantly over felsic and quartzose sedimentary rocks. The secondary cementation by quartz and hyalite (opaline silica) observed in many profiles is generally due to weathering under arid conditions. The ferruginous horizon is commonly most strongly developed over ultramafic and mafic rocks, tending to be thinner, less ferruginous and less strongly cemented over other lithologies and almost absent over granitoids. This is particularly evident in the inland, now semi-arid regions of the Yilgarn Block, and differs from other lateritic terrains in Africa and South America in which thick lateritic duricrusts (crairasses) are present even over granitoids.

4. *Retention and accumulation of immobile elements and stable minerals*

The distributions of Cr, K, Zr, Hf, Th, Nb, Ta, W, REE, Ti and V relate wholly or in part to their inertness during weathering, which is due to their chemical immobility (e.g., V, Ti) and/or to the stability of their primary and/or secondary host minerals (e.g., Zr and Hf in zircon; Ti in rutile and anatase; Cr in chromite; K in muscovite). Their abundances tend to increase upwards through the profile due to the gradual loss of other components, with marked accumulation in the ferruginous lateritic horizon, within which lateral dispersion by colluvial action has taken place during the course of profile evolution.

The distributions of Cr, Sc and Ga are closely interrelated with those of Fe and Al. In unweathered rocks, Cr and Sc occur together (and with Fe in chromite and ferromagnesian minerals), and Ga is associated closely with Al. These associations are retained throughout the saprolite, but some differentiation occurs with the development of the ferruginous horizon. Thus, Sc and Ga tend to be retained with Fe in the ferruginous horizon. Chromite is very resistant to weathering, so that contained Cr and Sc are almost immobile and have distributions similar to those of elements in other resistant minerals. Chromium in ferromagnesian minerals, however, is released in the ferruginous horizon and accumulates with Al in underlying clay-rich horizons. The distribution of As is also partly related to that of Fe, occurring preferentially in the ferruginous fractions of the lateritic soils and gravels and in more ferruginous samples deeper in the regolith.

5. *Minor redistribution of gold*

The behaviour of gold under lateritic conditions in Western Australia is unclear from most of the sites studied, due to its remobilization under later arid conditions. Evidence from humid lateritic environments in West Africa (e.g., Freyssinet et al., 1989a and 1989b) suggests that Au is essentially immobile throughout the saprolite but is chemically and physically dispersed in the lateritic horizons, to give widespread surficial haloes associated with the Fe oxide accumulations. Similar dispersion haloes are present in the lateritic Au deposits in the Yilgarn Block but, whereas in deposits such as Boddington and, in part, Mt. Gibson, the Au-Fe oxide association remains, at sites such as Bardoc, Callion, Mt. Percy and Mulline, there is a strong Au-carbonate association related to mobilization under semi-arid conditions. Nevertheless, relict primary Au particles in the ferruginous horizons and the extent of the secondary haloes are probably inherited from dispersion during lateritization.

1.3 INFLUENCE OF SEMI-ARID AND ARID CLIMATES

1.3.1 Principal characteristics

Characteristics commonly associated with weathering under arid conditions are those related to the excess of evaporation over precipitation, which result in the accumulation of otherwise soluble weathering products within the regolith, particularly near the surface.

1. *Accumulation of alkali and alkaline earth elements*

These typically concentrate in groundwaters and precipitate as carbonates, sulphates, halides and other salts in regoliths in semi-arid and arid regions. In lateritic regoliths in such regions, this results in the paradoxical accumulation of these highly mobile components in otherwise highly leached materials. This is exemplified in the southern Yilgarn Block by the concentration of Ca, Sr and, to a lesser extent, Mg and Ba as pedogenic carbonates and minor sulphates in the near-surface horizons, the precipitation of halite as a trace constituent throughout the regolith, local accumulations of alunite and the concentration of Br in clay-rich horizons.

2. *Secondary silica cementation*

Silica induration of various types is a common feature of the regolith in semi-arid Australia. It is considered to be post-lateritic, although the conditions of precipitation are poorly known. Massive silicification (as silcrete) was observed only at Mt. Percy, in the upper saprolite of the fuchsitic ultramafic rocks. Silicification of weathered ultramafic rocks commonly occurs over Al-poor lithologies (e.g., dunites at Mt. Keith, Agnew, Siberia - see Butt and Nickel, 1981) and is presumed to form because silica released during weathering is not leached and, in the absence of Al, cannot precipitate as kaolinite. Some of the fuchsitic ultramafic rocks at Mt. Percy are dunitic, but in the remainder, Al is unavailable due to the stability of muscovite. These silcretes are very stable and further chemical development ceases - i.e., once silicified, the saprolites cannot evolve to form mottled and pisolitic horizons. If silicification were a product of lateritic weathering, such horizons would not form. Accordingly, it is concluded that silicification probably occurred early during the post-lateritic period when the water-table was high, but the throughflow was insufficient to leach silica released by continuing weathering.

Silica cements the red-brown hardpans common in the northern part of the Yilgarn Block, e.g., at Youanmi (Report 23R), Bottle Creek, Cork Tree Well and Beasley Creek. Hardpans commonly consist of colluvium (of diverse provenance) and saprolite, cemented by hyalite (opaline silica). They are of recent origin; in places, silicification may be active but, in others, (e.g., Bottle Creek), the hardpan is disrupted by later carbonate precipitation.

3. *Development of smectites*

Smectitic clays tend not to form, or remain stable, in lateritic environments but are commonly found in regoliths in dry savanna and semi-arid climates. Here, they are most abundant (a) deep in profiles as intermediate products of the weathering of primary silicates occurring after the main period of lateritization, when leaching is insufficient to remove weathering products and the pH remains high, and (b) in depressions and valleys, where they precipitate directly from groundwater, following evaporative concentration of silica and alkalis.

4. *Erosion*

The Western Australian landscape has been modified by erosion, in part due to instability induced by vegetation changes during post-lateritic aridity. The erosion, by sheetwash, wind and minor drainage rejuvenation, has been insufficient to remove most of the debris, which has been redeposited on lower slopes and in valleys, further reducing the already low relief. However, aridity (and uplift) also resulted in the hardening and cementation of ferruginized horizons to form duricrusts that have protected the otherwise generally soft regolith. Silica cementation has had a similar role. Conversely, carbonate precipitation may assist erosion by disrupting, perhaps replacing, lateritic duricrusts and other surficial materials. Although carbonate cementation, as calcrete, may give some protection, this is only temporary, due to the solubility of calcite and dolomite. The resultant partly eroded landscape is a complex mosaic of variably truncated lateritic regoliths, with extensive tracts of transported cover.

1.3.2 Dispersion of minor and trace elements during arid weathering

Other than the accumulation of alkalis, alkaline earths and silica, discussed above, the change to aridity has not greatly affected the distributions of most elements in the regolith, since these are hosted by primary and secondary minerals that are stable in the weathering environment. However, the physico-chemical conditions of this environment have changed sufficiently to dissolve some stable resistant minerals, and weathering continues slowly at the base of the profile, so that minor dispersion still takes place. For example, base and transition metals (Cu, Co, Pb, Mn, Ni) are leached from upper horizons and precipitated in the mid to lower saprolite in Fe oxides or smectites. Similarly, at Mt. Percy, the absolute accumulation of REE in the lower saprolite is attributed to post-lateritic dissolution of primary minerals containing REE. The REE were later precipitated at a porosity barrier that may mark a past water-table, or underlie a perched water-table. At Mt. Pleasant, Lawrance (1988a) illustrated the dispersion of Cu, Zn, Mo, As and Au into recent alluvium overlying almost unweathered mineralization.

By analogy with lateritic regoliths in the humid tropics, aridity has affected the distributions of Au and Ag more strongly than most other elements. The principal effects include:

1. the occurrence of Au as Ag-poor secondary particles, particularly in the saprolite;
2. leaching and depletion of Au and Ag from some clay-rich upper horizons;
3. lateral dispersion of Au in the mid to upper saprolite;
4. the occurrence of Ag as secondary halides;
5. concentration of Au in pedogenic calcretes.

Items 1 to 4 are typical of those ascribed to mobilization of metals as halide (principally chloride) complexes under acid, oxidizing conditions in arid climates, whereas the accumulation of gold in pedogenic carbonates (Item 5) is a phenomenon as yet only reported from Western Australia, but which is probably characteristic of arid zones elsewhere.

1.4 GOLD DISPERSION DURING REGOLITH EVOLUTION

A model illustrating the dispersion of gold during lateritization and subsequent arid periods is shown in Figure 1.1). The main characteristics of this model have been described elsewhere (Butt, 1987, 1989a and b; Gray et al., in press); the present results support the model but have considerably extended understanding of Au mobility in arid environments. The chemical mechanisms of gold mobility in the weathering environment are discussed in Section 6.

1. During lateritization, oxidation at the weathering front commonly produces neutral to acid conditions, with a lower pH favoured particularly by the presence of sulphides. Gold in tellurides or held in the lattice of the sulphides and other minerals may be released, but the free metal remains largely immobile due to the absence of suitable complexing ligands: *thiosulphate* ions are not present, even at the weathering front, because they form only during sulphide oxidation in a neutral to alkaline environment, i.e., in the presence of excess carbonate, but such conditions do not appear to be common; *chloride* ion concentrations are low in groundwaters in humid climates; *organic* ligands are abundant in the near-surface horizons of the regolith but concentrations are very much lower in the saprolite. Nevertheless, some corrosion and reduction of size of Au grains occurs in the saprolite, probably due to complexing by organic ligands, but primary Ag-rich Au grains persist through the saprolite and into the ferruginous zone, and lateral dispersion into saprolitic wall-rocks is minimal.

Lateral dispersion of Au occurs in the ferruginous and mottled horizons, due partly to residual concentration and surface wash during land surface reduction, and in part to mobility as organic complexes, either in solution or as colloids. Some Au may also be contributed directly to the soil in organic litter after uptake by plants. Reduction of the complexes results in the incorporation of fine-grained Au with low Ag contents in Fe oxides, particularly in the lower part of the ferruginous horizon and in the mottled zone. Such mechanisms can account for the formation of lateritic Au deposits and Au anomalies, with their mixture of high and low fineness Au, that form widespread blankets over relatively narrow weathered mineralized sources. These lateritic haloes are present as relict features in Western Australian deposits (e.g., at Boddington; Davy and El Ansary, 1986), although many have been modified by, for example, the accumulation of some Au in pedogenic carbonate (e.g., Callion, Mt. Percy, Mulline).

2. With uplift and a more arid climate, the water-table is lowered, alkali and alkaline earth elements, derived from rainfall and continued slow weathering, are retained in the regolith and groundwaters become saline. The lowering of the water-table has probably been punctuated by still-stands or temporary rises due to reversals in climate. Such events have great significance, for the increased rainfall leaches precipitated salts and recreates redox conditions suitable for ferrolysis, thus producing acid and saline groundwaters. As these waters become more strongly oxidizing, they can become capable of dissolving Au and Ag as halide complexes. Evidence from Panglo (Report 125R) suggests that the Mn redox couple controls this oxidation step and that there, iodide is more important than chloride as the complexing species. During these humid periods, therefore, Au may be dissolved and mobilized, with precipitation taking place in response to a rise in pH or dilution of the halide concentration, both of which may occur when solutions percolating through the unsaturated zone reach the water-table. Precipitation is also caused by the reduction of the Au halide by ferrous iron, either at the water-table or at the interface between an upper oxidized aquifer and a lower reduced aquifer. The latter mechanism can account for enrichments parallel to, but below, the water-table (e.g., Panglo, Figure 4.4). These processes have probably occurred on several occasions, though not necessarily simultaneously at each site. Repeated strong leaching of the upper saprolite leads to the formation of the depletion zone between the lateritic and saprolitic enrichments of gold. Cycling of gold by plants under present day conditions may also cause depletion (see 4, below).

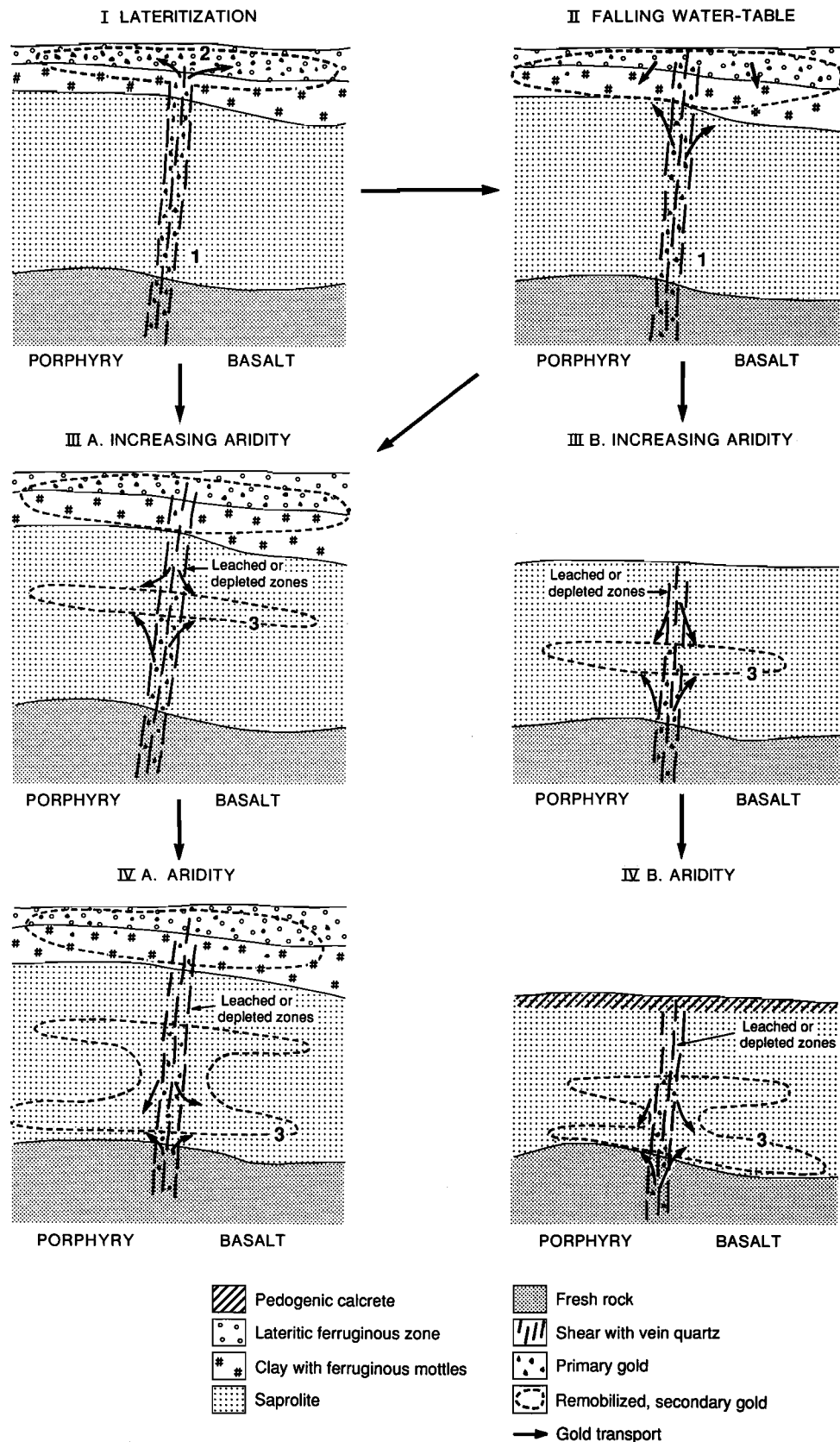


Figure 1.1

Model illustrating Au dispersion during lateritization and modifications due to uplift and a change to an arid climate. Ligands probably responsible for Au mobilization:- 1. thiosulphate; 2. organic; 3. chloride. (After Butt, 1989a)

3. Where the regolith has been truncated, any lateritic enrichment will have been removed. Irrespective of the relative timing of truncation and leaching, the ore zone may well be depleted at outcrop or sub-crop, so that the near-surface expression of mineralization is minimal.
4. Under present day conditions in semi-arid regions of the southern Yilgarn Block, the distribution of Au in soils is associated with that of pedogenic carbonates. The mechanisms of gold mobilization and precipitation, and the nature of the association with the carbonate, are not fully understood (see Sections 8 and 9). Dispersion probably involves cycling of Au via vegetation - by solution and uptake as an organic complex, mobilization by evapotranspiration, and deposition in litter. Calcium and Mg are similarly cycled via vegetation, and Au reprecipitates with these elements in pedogenic carbonates after release from the litter. This mechanism may also have contributed to the development of the depletion zone. The present field and laboratory research has shown that the association between Au and pedogenic carbonate is widespread in the southern half of the Yilgarn Block and that much of the gold is highly labile, implying that the dispersion is active under present conditions. The research has also demonstrated significant implications for exploration, since the Au - pedogenic carbonate association commonly gives a surface expression to mineralization even where the depleted zone outcrops or where there is a cover of transported overburden.

In semi-arid regions of the Yilgarn Block where soil carbonates are uncommon or absent, Au concentrations tend to be much lower and no other specific mineral or element associations with Au have been recognized. Dispersion and residence of Au in soils in these regions are to be investigated further in the successor project (Section 12).

2.0 REGOLITH TERMINOLOGY AND CLASSIFICATION

2.1 OBJECTIVE

The regolith comprises the entire altered, unconsolidated or secondarily recemented cover that overlies more coherent bedrock and that has been formed by the weathering, erosion, transport and/or deposition of older material. The regolith thus includes fractured and weathered basement rocks, saprolites, soils, organic accumulations, glacial deposits, colluvium, alluvium, evaporitic sediments, loess and other aeolian deposits. The regolith in deeply weathered terrains is particularly complex and may exhibit great variations in mineralogical and chemical composition, fabric and origin even within a single profile or toposequence.

Well-defined systems of terminology and classification are essential to provide an accurate description of regolith materials and units and to permit valid comparisons between sites. The regolith is polygenetic, hence descriptive attributes must recognize characteristics due to different events. The classification must be able to discriminate these characteristics accordingly and to emphasize those events considered to be the most important. In the Yilgarn Block and, indeed, in much of Australia, the regolith consists of a deep, mostly residual, lateritic weathering profile formed under warm, humid climates, modified by physical and chemical alterations induced by later tectonic and climatic changes (generally, uplift and a change to an arid climate). Accordingly, the terminology and classification are based on the fundamental characteristics of this profile, with modifications due to later events or features attributable to parent lithology added as descriptors. For example, the present-day formation of calcrete may, because of erosion, be superimposed on different horizons of the pre-existing profile. Classification of the product, therefore, may be either according to the later event (i.e., presence of calcrete) or to the earlier event (i.e., the horizon in which the calcrete has precipitated). The former recognizes a single "calcrete unit" and the latter subdivides the calcrete between the various horizons. The latter is the preferred classification but, in some circumstances, identification of the calcrete unit may be paramount, in which case the alternative classification could be adopted. Providing the descriptions of the material are adequate, classification according to either scheme should be possible.

The scheme described here is derived in part from the discussion paper compiled for Projects P240 and P241 (Anand and Butt, 1988). The terms conform, as far as possible, with established national and international usage. As in all natural systems, many changes are gradational, consequently the limits to some defined units are arbitrary (e.g., saprock). Similarly, the placement of some units can be equivocal and may depend upon the purpose of the classification, as discussed above for calcrete. Sedimentary units deposited on bedrock or pre-existing regolith are usually considered as part of the regolith. However, with respect to post-depositional weathering, the unaltered sediment could be regarded as the bedrock and the altered sediment as regolith. Such distinctions are rarely significant in exploration, although they arise in the Yilgarn Block where Permian glacial deposits and Tertiary sediments occur, e.g., in palaeodrainages.

2.2 THE LATERITIC REGOLITH

2.2.1 Classification

The classification and terminology adopted for this Project are summarized in Figure 2.1. The classification is broadly hierarchical, with sub-divisions of each unit defined in terms of a given set of attributes. Increasing sub-division requires a greater level of detail for correct classification. However, the detail and precision that can be achieved are limited by the sampling procedures and the nature and sophistication of the observations. Thus, samples obtained by rotary or percussion drilling cannot be described using the same set of attributes as those obtained by core drilling or from outcrop and hence cannot be classified with the same precision. For example, the "clay zone" as observed by rotary drill cuttings may include more than one horizon of the lateritic profile (e.g., saprolite and mottled zone) and show none of the distinctive fabric elements.

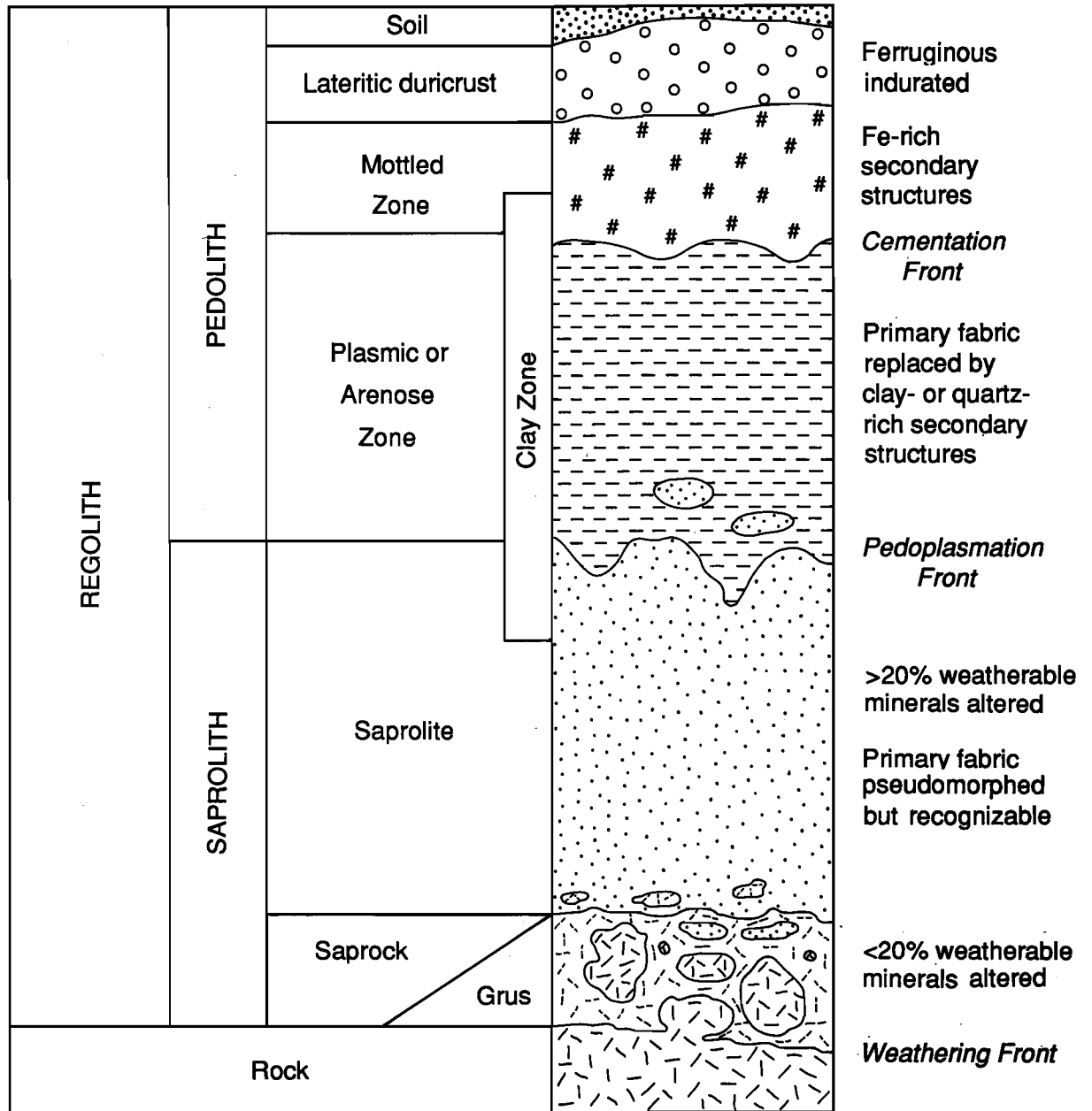


Figure 2.1 Regolith terminology

2.2.2 Principal units

The profile consists of two major components, the saprolith and the pedolith. These are distinguished by their fabrics, which, in turn, reflect their genesis.

Saprolith:

The (generally lower) part of the regolith that has retained the fine fabric originally expressed by the arrangement of the primary mineral constituents (e.g., crystals, grains) of the parent material. The definition may be extended to include weathered rocks in which only larger structures including bedding, schistosity, veining or lithological contacts are preserved. The presence of these fabrics implies that weathering has been essentially isovolumetric and pseudomorphic.

Pedolith:

The upper part of the regolith in which the fabric of the parent material has been destroyed by one or more pedological processes, including non-isovolumetric weathering associated with soil formation and/or the development of new fabrics. Some horizons of the pedolith are characterized by the concentration of particular elements (e.g., Fe and Al oxides in lateritic profiles) and the presence of distinctive secondary structures such as pisoliths.

The boundary between saprolith and pedolith is termed the *pedoplasation front*. Further subdivision is into the commonly recognized horizons of the lateritic weathering profile.

Saprolith

Only two saprolith horizons, saprock and saprolite, are recognized at present. Although the saprolite commonly comprises at least two thirds of a complete laterite profile, there is as yet no satisfactory procedure for further subdivision. The principal criterion for any subdivision should be a weathering index, but there is little agreement as to how such an index can be defined. These horizons may be developed on any rock type, although a distinctive variant, *grus*, resulting from considerable physical disintegration, may be present over granitoids.

Saprock:

A compact, slightly weathered rock of low porosity with less than 20% of the weatherable minerals altered. Weathering effects are present along mineral boundaries and intra-mineral fissures, along cleavages, shears, joints and fractures or affecting only a few individual mineral grains or mineral species.

Grus:

Fragmental disintegration product of largely unweathered granitic rock. Commonly applied to surface products, but also present as a porous horizon ranging from a few centimetres to 10 m or more thick at the base of the saprolite. Grus differs from saprock in that it is friable rather than compact.

Saprolite:

Weathered bedrock in which fine fabrics, originally expressed by the arrangement of the primary minerals (e.g., crystal, grains), are retained. Compared to saprock, more than 20% of the weatherable minerals have been altered. The definition may be extended to include weathered rocks in which only larger structures such as bedding, schistosity, veining or lithological contacts are preserved. Saprolite may become more massive upwards as the proportion of clay increases and cementation by secondary silica, carbonates, aluminosilicates and, especially, Fe oxides is not uncommon. The term "pallid zone" should not be used synonymously for saprolites for the latter exhibit a wide variety of colours. Although saprolites are commonly white over felsic rocks, over some felsic and most mafic and ultramafic rocks they are not; conversely, not all pale or white horizons are saprolite.

Recognition of saprolite in percussion and RAB drill cuttings may be difficult, particularly at shallow depths where the weathering has been very intense and the material is soft and clay rich, so that fabrics are easily destroyed by drilling. The "clay zone" seen in such cuttings may include saprolite, plasmic clay and mottled zone.

Pedolith

Subdivision within the pedolith is based on fabric, particularly those of the secondary structures, and/or on the concentration of particular elements. The principal horizons are the mottled zone, ferruginous zone (laterite) and soil. Generally, fabric loss and the accumulation of Fe and Al oxides appear to coincide fairly closely, defining the mottled zone. Where such accumulation occurs without fabric loss, the material remains classed as saprolite. Where fabric loss occurs without oxide accumulation, there is a transitional zone of settling and consolidation, the plasmic or arenose horizons, which occur just above the pedoplasation front at the base of the pedolith, between the saprolite and the mottled zone. Major structural features, such as quartz veins and lithological contacts, may still be preserved, generally with some change in orientation (dip).

Plasmic horizon:

Massive clays or silty clays, commonly having a mesoscopically homogeneous *plasmic* fabric, developed over rocks poor in quartz. The loss of lithic fabric is caused by solution and authigenesis of minerals and the mechanical processes such as shrinking and swelling of clays and settling of resistant primary and secondary minerals through instability induced by leaching.

Arenose horizon:

A sandy horizon having a grain-supported (or nearly so) fabric. The loss of lithic fabric appears to be caused by solution of weatherable primary and secondary minerals and settling of resistant minerals, dominantly quartz.

Mottled zone:

An horizon characterized by localized spots, blotches and streaks of Fe oxides that, with further mobilization and concentration, become reorganized into secondary structures such as pisoliths and nodules and that surround tubular voids (Plate 2.1 (b)). Nodule growth progressively destroys pre-existing fabrics, although lithic, plasmic or arenose fabrics and micro-fabrics may be preserved in the core.

NB. The definition of the mottled zone inherently includes fabric changes in the matrix and the development of secondary structures by the oxides themselves; colour variegation alone is not diagnostic. The mottled zone is part of the lateritic profile, probably formed at or above the water-table. As such, it is distinct from mottling associated with later weathering episodes, e.g., at lower water-tables or in soils formed on partly stripped profiles.

The pisoliths, nodules and voids (both open and infilled) of various shapes that develop in the mottled zone become upwardly more numerous. In the ferruginous zone (or laterite), they may either be cemented together to form an ironstone or duricrust, or become dominant over any intervening matrix.

Ferruginous Zone, "Laterite":

A highly weathered material, depleted in alkalis and alkaline earth elements, that is composed principally of secondary oxides and oxyhydroxides of iron (goethite, hematite, maghemite) and hydroxides of aluminium (e.g., gibbsite). These oxides may incorporate other minerals including clays and other secondary minerals (e.g., kaolinite, halloysite, anatase), resistant primary minerals (e.g., quartz, zircon, rutile) and weatherable primary minerals (e.g., ilmenite, muscovite). The laterite horizon is hard or subject to hardening upon exposure (definition after Sivarajasingham *et al.*, 1962).

Laterite may be either indurated or unconsolidated. *Lateritic duricrust* or *cuirasse* is indurated laterite composed of various structural forms of secondary segregations such as mottles, nodules, pisoliths and oololiths, cemented by a matrix of clay and aluminium and/or iron oxides. *Lateritic gravels* consist of unconsolidated ferruginous segregations and fragments. A classification of these materials has been developed by Anand et al., (1989) for Project P240.

Although lateritization is dominated by chemical weathering, physical processes (e.g., erosion by sheetwash) also occur, with sedimentation on plains and in valleys. These sediments, which may already be weathered and "lateritic", may then be reweathered. For sampling purposes, recognition of the sedimentary origin is critical and may require comparisons of immobile element and resistant mineral compositions of overburden and known residuum. Investigation of the degree of homogeneity of the fragments or clasts and of the characteristics of surface lag can assist with identification.

2.3 POST-LATERITIC MODIFICATION OF THE REGOLITH

2.3.1 Partial truncation

Erosion has occurred due to instability resulting from climatic change or drainage rejuvenation following uplift. Removal of the upper horizons of the profile results in the lower horizons, including unweathered rock, being exposed at the surface. The exposed lower horizon may outcrop, become the parent material of newly formed soils or be overlain by transported overburden. The erosion products occur as extensive transported overburden including alluvium, colluvium, sheet-wash, evaporitic sediments and aeolian material on fresh or weathered bedrock. These sediments may be friable or partially or wholly consolidated, cemented by iron oxide, silica, carbonates, gypsum or clays.

2.3.2 Cementation by introduced components

Cementation is one of the most recognizable modifications to a lateritic profile occurring in response to the change from a humid to an arid climate. The most common cements are iron oxides (ferricrete), silica (silcrete, hardpan), Ca and Mg carbonates (calcrete), aluminosilicates and gypsum.

Ferricrete:

Indurated material formed by the in situ cementation or replacement, or both, of pre-existing regolith by Fe oxides. The fabric, mineralogy and composition of ferricretes may reflect those of the parent (regolith) material and hence, if residual, the underlying lithology. Some authors restrict the term to the ferruginous horizon of lateritic regoliths (and therefore synonymous with *cuirasse*, *lateritic duricrust*) but the more general definition is preferred.

Silcrete:

Strongly silicified, indurated regolith components, commonly having a conchoidal fracture with a vitreous lustre. Silcretes appear to represent the complete or near-complete silicification of a precursor regolith horizon by the infilling of available voids with silica. They may be broadly subdivided into pedogenic or groundwater types. Most are dense and massive, but some may be cellular, with boxwork fabrics. The fabric, mineralogy and composition of silcretes may reflect those of the parent (regolith) material and hence, if residual, the underlying lithology. Thus, silcretes over granites and sandstones have a floating or terrazzo quartz fabric and tend to be enriched in Ti and Zr; silcretes with lithic fabrics (e.g., on dunites) are silicified saprolites with initial constituents diluted or replaced by silica.



Plate 2.1(a) Nodular and massive pedogenic calcrete, displacing and replacing lateritic gravels, Mulline.



Plate 2.1(b) Cementation front, Kanowna. Transition from upper saprolite to mottled zone.

Hardpan:

A near-surface indurated horizon. Red-brown hardpans, such as the Wiluna Hardpan, consist of a variety of transported or residual host materials, including colluvium, pisolitic horizons and brecciated saprolite set in a porous, red-brown earthy matrix, cemented by silica (generally as hyalite). The material has a coarsely laminated appearance and commonly has Mn oxides on partings. Wiluna Hardpan is generally 0.5-10.0 m thick, and is found N of about 30°S (the Menzies Line, Figure 1, p iii). It is commonly overlain by a red-brown, gravelly clay soil.

Calcrete:

A generally indurated material formed by the *in situ* cementation or replacement, or both, of pre-existing regolith by secondary carbonates. They vary widely in carbonate content and properties, from friable, fine grained soils to coarse nodular horizons to limestone rock. There are two principal genetic types, namely (1) pedogenic or vadose calcretes (Plate 2.1) and (2) groundwater or phreatic calcretes. Most consist of calcite and/or dolomite; magnesite occurs over some ultramafic rocks. Groundwater calcretes may have minor aragonite and Mg clays such as sepiolite. Pedogenic calcretes are most abundant to the south of 30°S (the Menzies Line, see Figure 1, p. iii), groundwater calcretes to the north.

2.3.3 Soil formation

The soils which originally overlay the developing lateritic profiles (ferralsols) are probably not preserved, although, it is possible that they have contributed to some of the extensive sand plains over granites. Most soils are developed from, rather than with, the material they overlie, whether these are the ferruginous zones of complete profiles or the exposed horizons (e.g., mottled zone, saprolite, fresh rock) of truncated profiles, and have characteristics inherited from these parent materials.

3.0 MINERALOGY, PETROGRAPHY AND GEOCHEMISTRY OF WEATHERING

3.1 MINERAL REACTIONS

3.1.1 Initiation of weathering

Water contains highly reactive hydrogen ions which are powerful weathering agents, as shown by several of the reaction equations that follow. Water has access to the rock along faults, joints and cleavages on a scale of metres to tens of metres, and high fluid flow rates are possible. Penetration of solid rock is more difficult. Initial access is along the margins of quartz veins and along intergranular boundaries, on the scale of a few mm, and fluid flow rates are slow. Access to the minerals occurs along mineral cleavages, twin boundaries and lattice dislocations on the scale of a few microns to nanometres, with minute rates of fluid movement, probably governed largely by diffusion. Thus, *initial* penetration of a fresh mineral is a slow process and its rate depends on factors such as mineral cleavage and strain. Weathering solutions etch tube-like channels that spread outward into a grain, improving fluid access and so accelerating the rate of weathering. Dissolved ions diffuse away from the weathering front, where they are in high concentration, to large voids and fractures, where they are in low concentration and come in contact with flowing solutions.

3.1.2 Weathering reactions

Weathering of igneous and metamorphic rocks consists of the conversion of a suite of high temperature *primary* minerals to a suite of new, low temperature *secondary* minerals stable in the weathering environment. This proceeds largely by oxidation and hydrolysis. The various components of the rocks are removed sequentially (e.g., see Section 1.2). The losses are shown by a decrease in the volume of the product minerals (reflected by v in Table 3.1), and a decrease in bulk density, and progressively increase the porosity of the rocks. This, in turn, allows improved fluid access and accelerates weathering, particularly in the saprolite. Some of this porosity is lost in the plasmic zone, where clay deposition and structural collapse take place, though vesicular structures locally increase porosity. Although weathering releases many elements into solution, new minerals are formed and these capture mobile elements by incorporating them into their crystal structures or by surface adsorption. Where cementation (by Ca, Si, Fe or Al) occurs, fluid movement decreases but weathering is then relatively complete.

Pyrite

Sulphide oxidation generally occurs at the weathering front and occurs in two steps, particularly if availability of oxygen is limited. First pyrite oxidizes and releases soluble Fe^{2+} , SO_4^{2-} and H^+ (Table 3.1, Equation 1). The acid conditions so produced may be locally buffered by decomposition of any carbonates present in the gangue and wall rocks, and by silicate weathering reactions that require a low pH to proceed. The second stage may be remote from the first, where oxygen is more plentiful, and involves the combined oxidation and hydrolysis of the Fe^{2+} to precipitate iron oxyhydroxides and release more protons (Table 1, Equations 2 and 3; see also Section 7.2). Apart from water, sulphide oxidation is a prime source of hydrogen ions for weathering reactions; thus, where oxidizing sulphides are present, weathering often proceeds to far greater depths than would normally occur. Oxidation of sulphides releases a very large suite of chalcophile elements.

Feldspar

Transmission electron microscopy by several workers (e.g. Eggleton and Buseck, 1980) has shown that feldspar weathering may be either (a), a single step reaction (i.e., directly to kaolinite) or (b), a two step reaction in which plagioclase feldspar converts to smectite (Table 3.1, Equation 4) and then the smectite alters to kaolinite (Table 1, Equation 5). Both are hydrolysis reactions, requiring a source of hydrogen ions (acid conditions), and release alkalis and alkaline earth elements. Potassium feldspar weathering proceeds similarly, though via illite (which may be expressed as a smectite with interlayered K) and occurs higher in the profile (Robertson, 1990). Development of smectite is commonly not seen in laterite profiles and may either not

occur or be a transitory phase, occurring only on the sub-micron scale. If the reaction for alkali feldspar (Table 1, Equation 6) is compared with that of calcic plagioclase (Table 3.1, Equation 7), more kaolinite is produced from the calcic plagioclase, resulting in a very compact kaolinite; the alkali feldspar loses more silica and results in a porous product (compare v values for Equations 6 and 7). Other elements released by feldspar weathering include minor Ba, Rb, Sr and REE and trace Pb, Ag and B.

Chlorite

Weathering of chlorite to smectite requires oxidizing, acid conditions and yields Fe oxides which cause turbidity in the chlorite (Table 3.1, Equation 8). The smectite then hydrolyses to kaolinite, requiring more hydrogen ions to do so and releases Fe and alkaline earth elements. Weathering chlorite releases minor Cr, Li, Mn, Ni and Ti. At Mt. Percy, chlorite is the principal host of Cr.

Micas

Muscovite seems first to lose its K, converting to illite or hydromuscovite, and then loses a Si tetrahedral layer (Robertson and Eggleton, 1991) and changes to kaolinite (Table 3.1, Equation 9). This is an hydrolysis reaction requiring hydrogen ions. Both Si and Al from the tetrahedral layer dissolve, later to combine and deposit elsewhere as more kaolinite (Table 3.1, Equation 10). This soluble Al could alternatively participate in the kaolinization of talc (Table 3.1, Equation 15). Weathering of muscovite releases minor Cr, F, Li, Rb, V and Ti, and traces of B, Cu, Nb, Pb, Sn, W and Zn. Weathering of biotite and phlogopite proceeds more readily than muscovite; biotite releases a similar element suite to muscovite, together with much Fe. Generally, the more complex the silicate, especially sheet and chain silicates, the richer and more varied their contained suite of trace elements.

Kaolinite

Halloysite is a common secondary mineral in Si-rich groundwater environments such as those in the Yilgarn Block. Kaolinite may hydrate to halloysite (Table 3.1, Equation 11). Sheets of kaolinite alter inhomogeneously to halloysite and so buckle and curl into spiral structures, much like a rolled newspaper (Robertson and Eggleton, 1991). This type of halloysite is generally Fe-poor, but smaller halloysite tubes contain more Fe (about 2%) and very Fe-rich halloysites tend to a spherical morphology. Near the coastal margin of the Yilgarn Block, where rainfall is more plentiful and drainage more effective, the groundwater is poor in Si so that kaolinite dissolves and gibbsite is precipitated (Table 3.1, Equation 12) with silica removed by the groundwater. Some kaolinite in upper parts of the profile, above the pedoplasation front, may dissolve and precipitate elsewhere, causing extensive fabric changes (Table 3.1, Equation 13).

Tremolite and talc

Both these magnesian minerals contain little Al. Although both require significant quantities of hydrogen ions to weather, their weathering behaviour is markedly different. Tremolite dissolves near the base of the profile (Plate 3.1), leaving hollow voids, and releases alkaline earth elements and Si to solution (Table 3.1, Equation 14). In contrast, talc remains stable to near the top of the profile and then weathers to kaolinite (Table 3.1, Equation 15; see Plate 3.1), but for this it requires an external source of Al ions, possibly supplied by weathering of muscovite and kaolinite. Talc and tremolite have fairly simple compositions and release Mg, Ca, Fe, Si and traces of Ti.

Hornblende

Hornblende and other amphiboles alter to smectite deep in the profile and thence to kaolinite higher up. Alteration begins along the amphibole cleavage and is generally nearly complete before chlorite is attacked (Report 58R). Weathering of amphiboles, particularly hornblende, may release small amounts of Cr, Cu, F, K, Li, Mn, Ni, Sn, Ti, V and Zn.

Table 3.1 Mineral equation reactions***Pyrite***

- 1) $2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+$
pyrite
- 2) $2\text{Fe}^{2+} + 0.5\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{Fe}^{3+} + 2\text{OH}^-$
- 3) $2\text{Fe}^{3+} + 6\text{H}_2\text{O} \rightarrow 2\text{Fe}(\text{OH})_3 + 6\text{H}^+$
goethite

Feldspar

- 4) $4\text{Ca}_{0.5}\text{Na}_{1.5}(\text{Si}_{5.5}\text{Al}_{2.5})\text{O}_{16} + 8\text{H}^+ + 16\text{H}_2\text{O} \rightarrow$
plagioclase
- $4\text{Ca}_{0.25}\text{Al}_2[\text{Si}_{3.5}\text{Al}_{0.5}]\text{O}_{10}(\text{OH})_2 + 6\text{Na}^+ + \text{Ca}^{2+} + 8\text{H}_4\text{SiO}_4$
smectite

 Δv 100:87

- 5) $4\text{Ca}_{0.25}\text{Al}_2[\text{Si}_{3.5}\text{Al}_{0.5}]\text{O}_{10}(\text{OH})_2 + 2\text{H}^+ + 13\text{H}_2\text{O} \rightarrow$
smectite
- $5\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{H}_4\text{SiO}_4 + \text{Ca}(\text{OH})_2$
kaolinite

 Δv 100:79.***Alkali Feldspar***

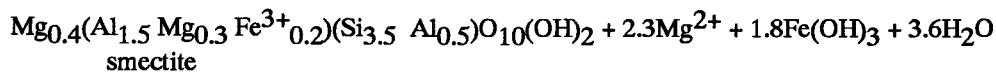
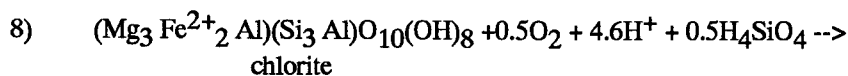
- 6) $2[\text{Na},\text{K}]\text{AlSi}_3\text{O}_8 + 9\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2[\text{Na},\text{K}]^+ + 4\text{H}_4\text{SiO}_4$
alkali feldspar kaolinite

 Δv 100:49***Calcic Plagioclase***

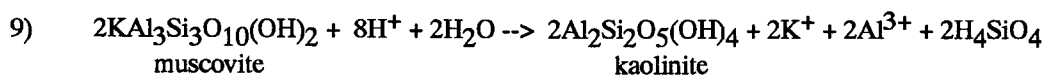
- 7) $2\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}_2\text{O} + 4\text{H}^+ \rightarrow 2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Ca}^{2+}$
anorthite kaolinite

 Δv 100:98

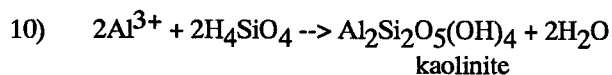
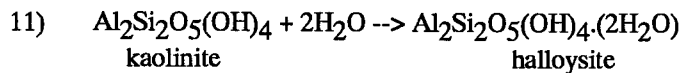
Table 3.1 Mineral reaction equations (continued)

Chlorite

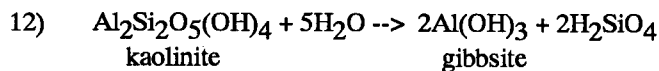
$$\Delta v \sim 100:87$$

Muscovite

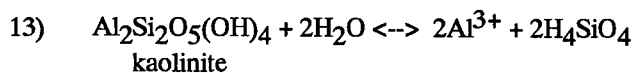
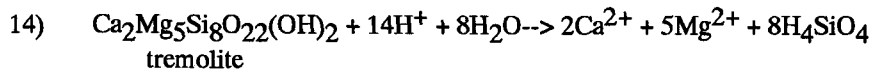
$$\Delta v 100:70$$

**Kaolinite**

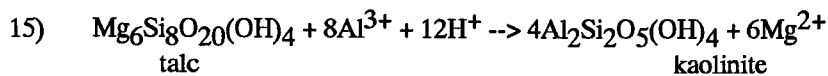
$$\Delta v 100:116$$



$$\Delta v 100:49$$

**Tremolite**

$$\Delta v 100:0$$

Talc

$$\Delta v 100:101$$

Carbonates

Primary carbonates (siderite, ankerite, dolomite and calcite) all weather at the base of the profile. If this occurs with sulphide oxidation, the breakdown of excess carbonates tends to buffer the reaction, keeping the pH neutral (see Section 6.2). Calcium, Mg, Fe and traces of Mn, Sr and Ba are released on weathering. Iron and Ba tend to be retained as Fe oxides and barite respectively, but most Mn and Sr are leached from the profile.

3.1.3 Secondary minerals

Though a few minerals remain unaffected or relatively so (such as quartz, chromite, rutile and zircon), weathering generally produces a range of new minerals. The most abundant are the clays (kaolinite, its hydrated equivalent, halloysite, and smectites) together with Fe oxides (goethite, hematite and maghemite), several Mn oxides (commonly pyrolusite, cryptomelane and lithiophorite), cryptocrystalline or amorphous silica, and carbonates. A number of secondary carbonates and hydroxy-carbonates may be formed from Ca, Mg, Fe, Mn, Sr, Ba, Bi, Cu, Ce, La, Pb, U and Zn. Some secondary minerals can adsorb, or incorporate into their lattices, significant quantities of trace elements released by weathering. Most important of these are the Fe oxides, which may concentrate Ag, As, Bi, Cr, Cu, Mn, Ni, Sb, Se, Ti and Zn; the Mn oxides adsorb Ag, Ba, Co, Cu, Ni, Pb, Sb, Li, W and Zn. The high sorption capacity is due to the very high surface areas; for example, goethite generally has a very small crystal size (about $0.03 \mu\text{m}$) and hence a very high surface area (about $100 \text{ m}^2/\text{g}$). Smectites have a high ion exchange capacity and, apart from Si and Al, are able to incorporate significant amounts of Fe, Mg, Zn, Mn and Ni variously in octahedral and tetrahedral sites. The exchange cations are Ca, Na, K, Cs, Sr and Mg; the exchange capacity varies with the type of smectite and the physical conditions. Ions of a greater valency (e.g., Ca) are more readily retained. Kaolinite has only about 2% of the capacity of smectite to hold other ions.

3.2 MINERAL STABILITY

Mineral stability in the weathered profile is illustrated by using the Rand Pit, Reedy (Plate 3.1) as an example, supported by evidence from other deposits, especially Panglo, Mt. Magnet and Mt. Percy.

Chlorite is an important component of many mafic and ultramafic rocks. At Reedy it is particularly abundant in the lower two thirds of the profile, where it is closely associated with the cleavage. Further up the profile, but still within the saprolite, *smectite* progressively replaces the chlorite. This is particularly marked where sulphides in the ore shoots have oxidized, causing an acid environment that enhances the breakdown of chlorite, so promoting weathering to great depth. Higher in the saprolitic profile *kaolinite*, in turn, replaces smectite. In contrast, at Mt. Percy, chlorite appears to weather directly to kaolinite, without intermediate smectite, though smectite probably occurs as a transitory phase. The chlorite at Mt. Percy is the principal host to chromium and the resultant kaolinites are green.

Feldspar is an important primary mineral in both the mafic rocks (plagioclase) and in the porphyries where it occurs as albite, microcline and microcline perthite. Plagioclase degrades readily to kaolinite deep in the saprolite but, although microcline survives higher in the profile, it also ultimately weathers to kaolinite.

Talc is a very resistant mineral and may survive to the upper saprolite or mottled zone, so that it is a useful indicator of ultramafic rocks. It weathers in part to kaolinite but, as it contains little Al, a source of soluble Al is needed before this reaction can occur. *Tremolite*, another indicator of ultramafic rocks, weathers readily and is completely dissolved near the base of the weathering profile.

Muscovite generally persists throughout weathering profiles, as shown at Reedy (Report 102R), Mt Magnet (Report 33R) and Mt Percy, where it occurs as fuchsite (Report 156R). At Beasley Creek, flakes of muscovite from the ore host rock, partly altered to hydromuscovite, occur even in the ferruginous components of the

duricrust and overlying lag, where they are set in, and apparently protected by, goethite. Muscovite may partially weather to kaolinite in or just below the lateritic cuirasse (Reedy, Mt. Percy). Apart from being rock-forming minerals, micas (muscovite, paragonite or fuchsite) are important components of phyllic alteration haloes around mineralization (especially Beasley Creek, Mt. Percy and possibly Mt. Magnet) and their survival has exploration implications.

Primary *carbonates* occur near the base of the profile where they may form either part of an alteration halo or be due to widespread greenstone carbonation. They are absent from all but the top of the profile, where they reappear as secondary carbonates (calcrete and pedogenic soil carbonates). Likewise sulphur-bearing minerals such as *sulphides* are consumed at the base of the profile but sulphates (barite, gypsum and alunite) appear within the regolith. Deposition of secondary carbonates and sulphates is not linked to a particular part of the lateritic profile and deposition, except for some barite, appears to be a late event. Alunite has a greater depth range than gypsum.

Kaolinite and *goethite* are the ultimate products of a number of primary minerals (sulphides, pyroxene, amphibole, feldspar, chlorite, talc and muscovite). They are stable throughout the weathered profile, though kaolinite may dissolve and reprecipitate in the plasmic zone, producing much of the observed fabric changes characteristic of this zone; iron oxide cements are important in the mottled zone and duricrust. *Quartz* is also stable from fresh rock and through the weathering profile, though quartz grains become progressively corroded and siliceous cements are important near the top of the profile on some rocks.

Some minerals, such as *chromite* and *zircon* are particularly stable and survive virtually unaltered to the top of the profile. However, etched zircons occur in silcretes in the arenose zone over granite (Butt, 1985) and chromite weathers very slightly in the lateritic duricrust. *Rutile* is stable but other Ti-rich minerals such as *sphene*, *ilmenite* and *titanomagnetite* weather to *anatase*, which in itself is stable. Thus Cr, Zr and Ti are among the most geochemically stable elements (see below) but their behaviour is very dependent on the minerals that contain them.

3.3 WEATHERING FABRICS

3.3.1 Introduction

Fabric changes in a weathering profile are only one of the consequences of the reactions between weathering minerals. Although some secondary minerals replace their precursors, pseudomorphing and thus preserving the fabric, others dissolve and reprecipitate elsewhere, causing the greatest fabric changes. Pseudomorphic replacements tend to dominate the lower part of the profile where original rock fabrics tend to be well-preserved, defining the saprock and saprolite. Pseudomorphic replacements of feldspar by kaolinite or gibbsite, and pyroxene or amphiboles by goethite, leave the original rock fabric perfectly preserved or even accentuated. Fabrics are best preserved where the sizes of the elements of the original fabric are significantly greater than the crystal sizes of the replacing minerals.

Above the pedoplasation front, where pedogenic processes are dominant, mineral dissolution and distant precipitation are important and fabric changes become more marked. Such changes involve dissolution of clays, the formation of clay blasts, clay accordion structures and quartz segregation fabrics, the development of vesicular structures and channelways and the appearance of root casts, which become infilled with fragments from higher levels in the regolith. Pedoplasation tends to be incomplete and pockets of the original fabric may be found preserved very close to the surface. The importance of these processes increases into the mottled zone and laterite where segregation, concentration and cementation by Fe oxide minerals occur. The Fe oxides, chiefly goethite with some hematite and maghemite, replace and so preserve the plasmic and any surviving saprolitic or primary structures.

Fabric changes are illustrated by profiles over mafic and ultramafic rocks, granitoid porphyry, argillaceous metasediments and quartz veins from Rand Pit at Reedy (Report 102R), which were truncated near the base of the mottled zone. This is supplemented with fabric information from the duricrust and lag at Beasley Creek (Reports MG 67R and 27R).

3.3.2 Mafic rock

The fresh, schistose mafic rocks at Reedy consist of albite, chlorite, talc, muscovite, some metamorphic quartz and minor sulphides. The first change is oxidation of sulphides to iron oxides which defines the weathering front. Plagioclase alters pseudomorphically to kaolinite a short distance above the weathering front, but the original fabric remains. Slightly higher in the profile, chlorite, which depicts the rock cleavage, is partly altered to smectite, releasing Fe oxides. Although all minerals but quartz are altered, the original schistose fabric remains.

Above the pedoplasation front, some more fundamental changes occur. Pockets of fine-grained kaolinite develop which sweep the quartz granules into patches, so progressively destroying the schistose fabric. Vesicles, some linked by channels, provide ready access for water. Some vesicles and channels are hollow, others are lined or are completely blocked with clays. Some of these channels were etched by percolating solutions, others probably mark old root casts. The mafic-derived lag at Beasley Creek has smectitic "fingerprint" fabrics pseudomorphed by goethite.

3.3.3 Ultramafic rock

The fresh, schistose ultramafic rocks at Reedy (Plate 3.1) consist of matted talc and needle-like tremolite, cut by a chloritic cleavage with lenses and granules of metamorphic quartz. Again, sulphides weather to Fe oxides at the weathering front. A little higher in the profile, tremolite has dissolved, leaving needle-like voids that are filled or partly filled with goethite.

Talc is a resistant mineral that tends to survive through much of a lateritic profile, preserving the rock schistosity and raising the pedoplasation front. Where talc weathers, it is replaced by fine-grained kaolinite, but this tends to recrystallize into stumpy stacks and accordion structures, ultimately destroying the rock schistosity. Channelways, vesicles and cavities develop in the plasmic zone and can be filled with fragments from the regolith above. Typical stumpy stack and accordion fabrics are preserved as goethite pseudomorphs in the lag at Beasley Creek, though some goethite pseudomorphs after smectite also survive.

3.3.4 Granitoid porphyry

Unweathered porphyries at Reedy consist of varying proportions of xenomorphic plagioclase surrounded by granoblastic quartz and granules of late microcline-perthite. Many are slightly schistose, have suffered granulation and contain microxenoliths. Pyrite is the first to weather to hematite pseudomorphs. Plagioclase, including that in perthite, is the first silicate to weather and this is generally complete quite deep in the profile. Higher, the microcline also weathers to kaolinite, leaving a non-schistose rock of kaolinite and shard-like quartz; a micrographic fabric, preserved by quartz, may be all that can be recognized.

3.3.5 Black shales and mica schists

Fine-grained, argillaceous metasediment at Reedy consist largely of quartz and mica with minor graphite, talc and chlorite. Chlorite alters readily to smectite and then to kaolinite. Muscovite partly weathers higher in the profile but some survives, along with talc. Graphite is partly bleached in the upper part of the profile. At Beasley Creek, where these rocks have been intensely ferruginized at and near the surface, mica is preserved as relicts in goethite and fragments of this material occur in the lag.

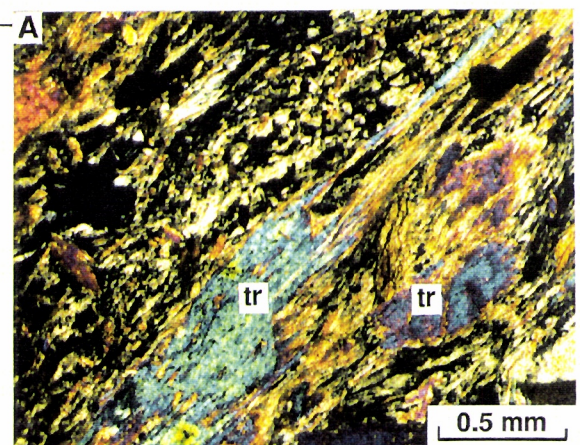
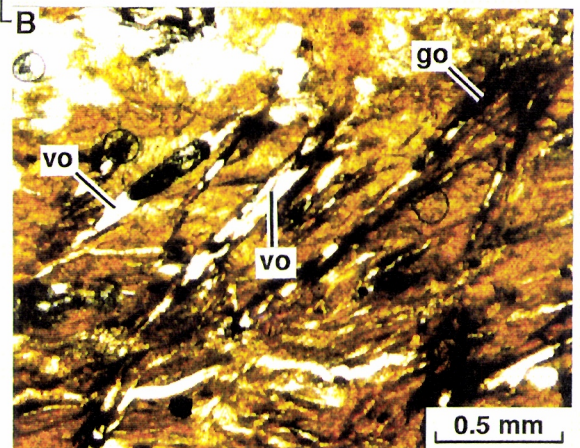
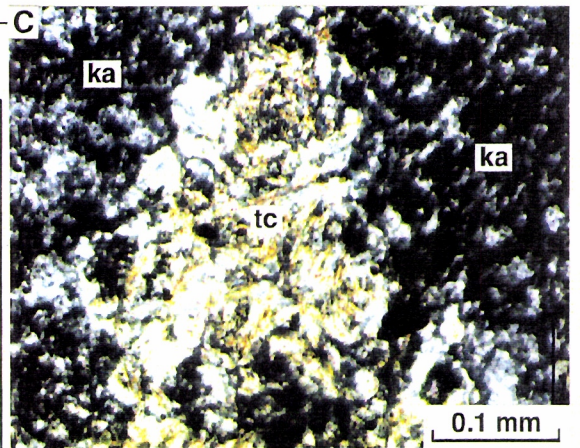
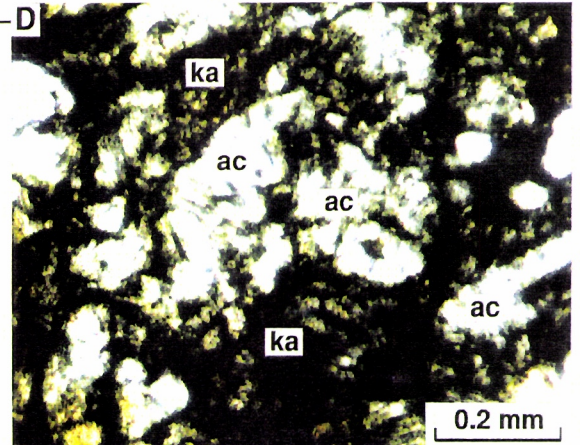


Plate 3.1 The 75 m thick regolith in the Rand Pit, Reedy, developed on porphyries and mafic, ultramafic and metasedimentary rocks. Changes in mineralogy and fabric are illustrated by the ultramafic schists. A: fresh schist consist of talc and tremolite (tr) cut by a chloritic cleavage. B: tremolite is one of the first minerals to break down, dissolving to leave acicular voids (vo), filled or partly filled with goethite (go). C: talc (tc) survives to high in the profile and so preserves the schistose fabric, but much is ultimately altered to kaolinite (ka). D: the kaolinite recrystallizes to accordion structures (ac), progressively destroying the original fabric.

3.3.6 Vein quartz

Vein quartz generally consists of angular, interlocking, sutured granules with individual crystals showing strain. Weathering solutions initially penetrate and etch the grain margins, loosening them. The vein takes on a sugary appearance and is generally stained brown by Fe oxides or clays deposited between the grains. Above the pedoplasation front, this clay or Fe oxide deposition progresses, the quartz granules drift apart, progressively losing their orientation and the vein loses its coherence.

3.3.7 Mottled zone, duricrust and lag

The petrography of ferruginous materials (mottled zone and duricrust) has been intensively studied by CSIRO/AMIRA Project P240. Some features can be seen in lag fragments (e.g., Beasley Creek, Report 27R) and in the underlying saprolite (Report MG67R). The upper saprolite consists of an assemblage of secondary and resistant primary minerals and many of these have been pseudomorphically replaced by goethite in the mottled zone. Micas appear to have largely resisted this process, though they have suffered some degradation in crystallinity and small-scale penetration by Fe, accompanied by loss of some K and minor hydrolysis to form illite. There were several cycles of later solution and redeposition of Fe oxides that have, in turn, partly replaced the pseudomorphed saprolitic fabrics with spongy goethite and formed cutans on some fragments. Higher in the mottled zone, red and brown ferruginous clays, surrounding the Fe-oxide-rich nodules, have been dissolved and redistributed as void fillings and cutans. The nodules themselves protected or partly protected their contained saprolitic fabrics from further dissolution, compaction and resultant distortion.

At or near the top of the ferruginous horizon, solution of clays and goethite occurred along fractures to form vesicles, with goethite later precipitated in the fractures and surrounding clays. Clay-rich hardened mottles became pisoliths by the solution and replacement of clays by Fe oxides, leaving a gravelly product. Near the surface and in the soil, some vesicles became filled with Fe oxides, clays and opaline silica. Erosion of the fine fractions by deflation and sheetwash has exposed the nodules which now contribute to the lag. Finally, at the surface, clay coatings were largely removed and some lag particles developed a desert varnish. Thus, there was a progression from the saprolite, via cycles of clay and Fe oxide replacements, to a ferruginous horizon. This became hardened during the post-lateritic arid period and contributed to a soil that has subsequently been eroded to produce lag.

3.4 MAJOR ELEMENT GEOCHEMISTRY

Dispersion in the regolith is discussed in Sections 1.0 and 4.0. The inter-relationships of the three major elements Si, Al and Fe as weathering proceeds can be shown in a ternary diagram. The profile at Beasley Creek (Report 152R) is used as an example. The fresh and relatively fresh amphibolitic footwall rocks form a coherent group (Figure 3.1) with the saprolites formed from them, indicating little geochemical change to the distribution of major elements apart from removal of the alkalis and alkaline earths. The clay zone rocks, corresponding approximately with the plasmic zone, though probably including parts of the upper saprolite and lower mottled zone, show a trend suggesting some Si loss and a gain in Fe. Loss of Si is typical of the plasmic zone, where quartz is partly dissolved and the proportion of Al thus increases. The trend towards Fe indicates early ferruginization in the mottled zone. If the mottled zone rocks and the duricrust are added to the ternary plot (Figure 3.2), a continued trend is seen, first towards Fe, as ferruginization becomes important, and then a trend towards Al as Si is dissolved. Gibbsite has been found in some of the duricrust samples at Beasley Creek.

3.5 ROCK TYPE DISCRIMINATION

3.5.1 Introduction

There are several means of discriminating rock types in the weathered profile, including colour, fabric, mineralogy and geochemistry. Geochemical changes that take place in a rock are complex, but probably geochemistry shows the most promise of all, particularly if a suite of elements is considered and processed as a multivariate data set. Ore-related elements should be excluded since these tend to confuse the rock type discrimination. It is best to interpret a combination of fabric, geochemistry, colour and mineralogy which, with experience, gives the best possible conclusion.

3.5.2 Colour

Colour variations are impressive in weathered rocks but are rarely diagnostic of lithology or weathering horizon. They are also very dependent on the ambient light conditions at the time, on experience and colour perception. The colours white (kaolinite, talc), red, yellow (Fe oxides), green (smectite, Cr, Ni or Fe^{2+}) and confusing mixtures of these result in inaccuracy and personal bias. Classification of colours using the Munsell system can be used to standardize terminology, but it cannot be used satisfactorily by those with defective colour vision. Spectrometry in the visible to short-wave infrared is perhaps more precise and can distinguish some minerals. Colour is generally leached, together with the transition elements that produce it, in the so-called 'pallid zone'.

3.5.3 Fabric

Fabric is very useful in fresh rock, saprock and much of the saprolite for identifying lithologies but its value is diminished where the weathered rock has been largely pulverized by drilling. Above the pedoplasation front, fabrics are altered by pedogenic processes. However, relict fabrics survive in places, because of incomplete pedogenic processes, or have been protected from pedogenic action by extensive ferruginization. Interpretation of weathered rock fabrics takes time and requires experience. Such experience is often lacking in those to whom drill logging is generally entrusted; such staff could be greatly assisted by an atlas of rock weathering, planned for the continuation project.

3.5.4 Mineralogy

Where weathering has been intense, kaolinite and Fe oxides, in many instances, are the end products of weathering of mafic and felsic rocks. Relict talc and muscovite help to identify ultramafic rocks, argillaceous metasediments or alteration zones, but separating them, in a fine-grained state, from kaolinite can be extremely difficult. X-ray diffraction or infra-red spectrometry are the only certain means.

Micas occur as part of the halo around mineralization at Mt. Percy (fuchsite), Beasley Creek, Rand, Mt. Magnet and Panglo (muscovite) (Reports 102R, 143R, 171R and 156R), where they persist throughout most of the saprolite and mottled zone, being significantly weathered only in the duricrust. Remnants of micas have been found preserved in ferruginous nodules in the saprolite and at the surface at Beasley Creek (Reports MG67R and 47R) but this preservation is generally accompanied by partial loss of their contained alkalis. Although muscovite occurs within both barren and mineralized weathered shales at Panglo, the sodic mica, paragonite, is much less abundant in mineralized shale profiles (Reports 32R and 171R). Paragonite is associated with unmineralized profiles at Mt. Magnet also and may be a negative indicator of mineralization.

Carbonates may be associated with alteration zones around mineralization. They may be significant deep in the profile (Reports 32R, 156R), but are readily destroyed near oxidizing sulphides. Pedogenic carbonates and calcretes occur near the surface and are related not to mineralization but to Ca-rich, and, some Mg-rich

rocks, and specific parts of the landscape (Reports 24R, 143R, 152R and 156R). However, the occurrence of carbonate near the surface has an additional exploration significance as a sampling medium (see Section 8).

Concentrations of S over ore have been noted in the coarse, ferruginous soil fraction at Beasley Creek and in the underlying saprolite, occurring as gypsum and minor barite at Beasley Creek and Mt. Magnet (Reports 27R, 33R, 105R and 152R). Alunite occurs in the mid to upper saprolite at Mt. Percy (Report 156R), Panglo (Report 32R) and Bottle Creek (Report 36R) and its analogue, jarosite, is noted in the gossans at Bottle Creek (Report 36R). Although S is a labile component and may have been introduced into the landscape as aeolian gypsum (see discussion in Report 156R), there are, in some instances, close spatial relationships with underlying weathered sulphides. These clearly require more field and some isotopic investigation.

Microprobe analysis of the Cr contents of rutile, mica, chlorite and, where present, spinel may be used to indicate original ultramafic, mafic or felsic bedrocks. Proximity to mineralization may be indicated by a decrease in Fe content in tourmaline and mica, and a decreased Na content in the mica (Reports 147R, 171R).

3.5.5 Geochemistry

During the course of the geochemical investigations, a number of elements emerged as rock-type identifiers. These may be used singly, in pairs, in threes and in n-dimensional space by multivariate (e.g. discriminant) analysis. As the number of elements used increases so too, to a limiting degree, does the reliability of discrimination.

Elements such as Cr are enriched in ultramafic rocks at Reedy, but Mg, Co and Ni are less effective because they are leached (or even enriched) in the upper parts of the profile (Reports 102R and 143R). Similarly the ultramafic rocks at Mt. Percy have high concentrations of Cr, V and Sc (Report 156R). Felsic rocks at Reedy are rich in Al, Ga and Zr but metasedimentary rocks vary considerably in their compositions due to their differing provenances. Thus single elements show considerable overlap, have only local application and their use may be severely limited to particular parts of the weathered profile.

Bivariate plots (element pairs) are slightly more successful. The most useful is Ti-Zr (or Ti-Hf) which is discussed in detail below. Metasedimentary rocks at Reedy (Report 102R) could be distinguished from mafic/ultramafic and felsic metavolcanic rocks by their Al-Ga relationships, though this separation is not distinct near the top of the profile. Some success was obtained with Rb-Nb, Rb-Sc and Rb-Li plots to separate the mafic-ultramafic suite from the metasedimentary and felsic suites. Partial discrimination was achieved between unweathered ultramafic variants (talcose, chloritic, biotitic and fuchsitic) at Mt. Percy (Report 156R) using plots of Ba, Zr and K. Metasedimentary ore host rocks at Beasley Creek are distinguished by high Mn, Ba and some rare earth elements (e.g., La and Ce). However the use of Ba, K and Rb also reflect mineralization, which tends to confuse the discrimination. Some trivariate plots of various combinations of Cr, Rb, Ga, Ti, Sc, Co and Zr were used to gain further improvements in rock type discrimination (Report 102R).

Ti, Zr and Cr

The three elements Ti, Zr and Cr are considered to be among the most stable in the weathered environment (Hallberg, 1984) but their effectiveness depends on the stability of their host minerals. Zirconium is largely held in zircon, which is generally quite stable. The presence of leached, skeletal zircons and, conversely, reports of the presence of overgrowths on zircon, indicate that even zirconium can become mobile under certain circumstances. Titanium is held in rutile, ilmenite and sphene and, when the latter two are weathered, their weathering products are stable Ti oxides (anatase and rutile). However silicates, notably amphiboles and chlorite, also contain significant quantities of Ti and these are highly weatherable. If Cr is held in chromite it is relatively stable but if it occurs in silicates such as fuchsite (chromian muscovite), pyroxene, chlorite or amphibole, it is readily released by weathering.

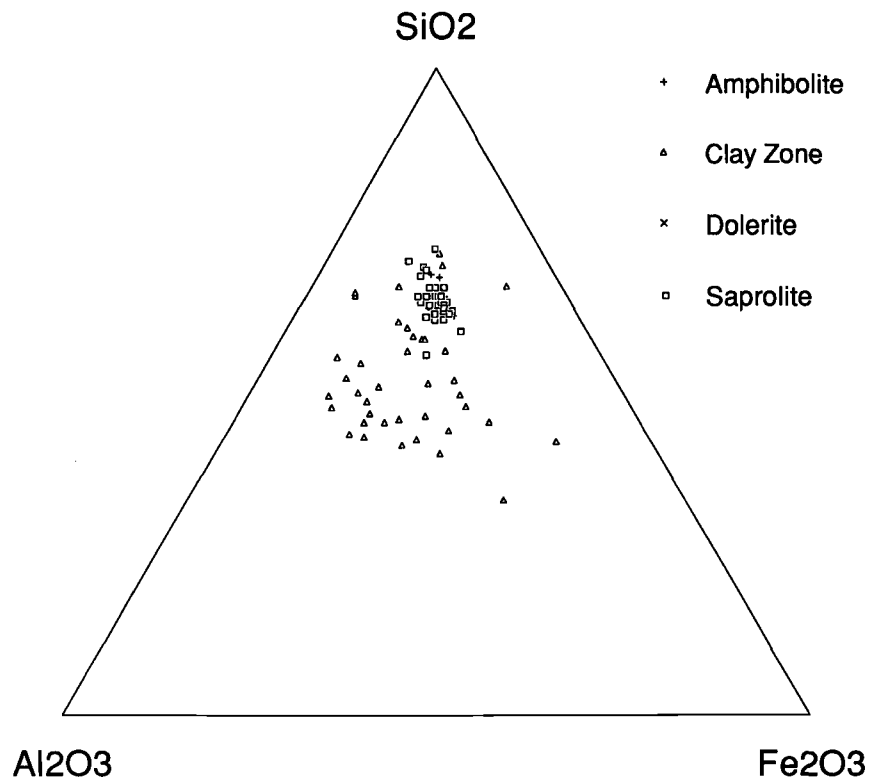


Figure 3.1

Major element compositions of fresh and weathered rocks, Beasley Creek. The compositions are closely grouped in the fresh rocks and saprolites, becoming more Fe- and Al-rich in the clay zone.

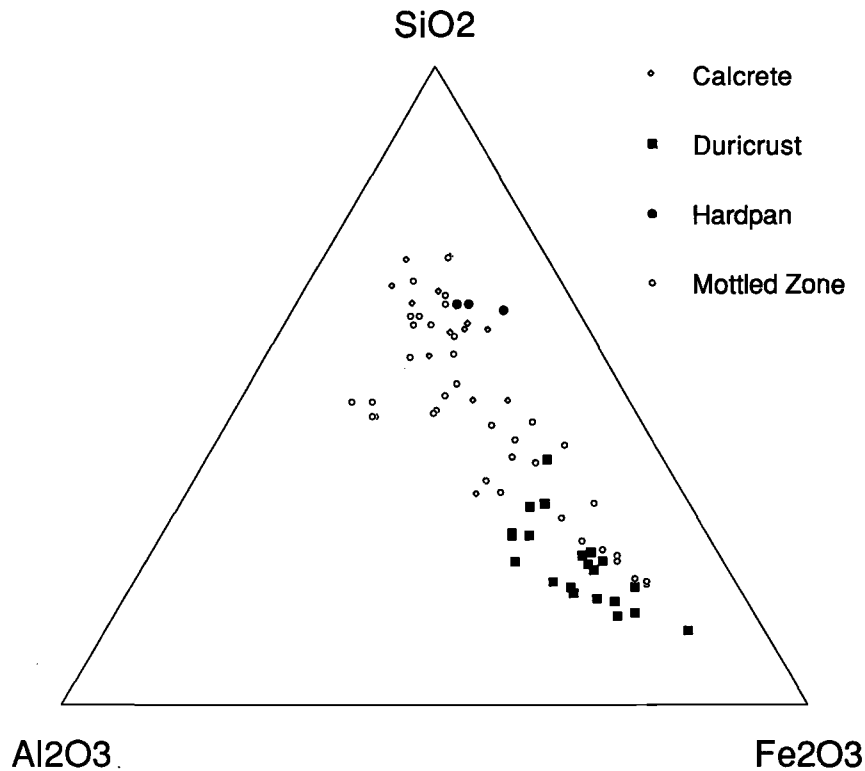


Figure 3.2

Major element compositions of principal surficial materials, Beasley Creek. The high Al and Fe contents of the mottled zone and duricrust extend the trend evident in the clay zone (Figure 3.1). The higher Al content of the duricrust is probably due to the loss of Si.

Hallberg (1984) showed that the major groups of igneous rocks could be distinguished, even in the weathered state, by the Ti/Zr ratio. Basalt has a Ti/Zr ratio of greater than 60, andesite ranges from 60-12, dacite from 12-4 and rhyolite is generally less than 4. Inevitably, the fields show some overlap. The ultramafic rocks have a similar Ti/Zr ratio to basaltic rocks, but are richer in Cr. At Mt. Percy (Report 156R), it was possible to distinguish the unweathered porphyries from the ultramafic rocks on their Ti and Zr contents. This method of distinction also works well for moderate weathering in the saprolite and the clay zone as illustrated by a data set from the footwall rocks of Beasley Creek (Report 152R), where most of the rocks approximate to a basaltic composition. However, if the saprolites and clay zone rocks are plotted separately from the surficial materials, it is clear that much of that part of the field with low Ti/Zr is near-surface material. Thus, this method has limited application in the mottled zone and in the duricrust where Ti is only partly stable.

The ultramafic and mafic rocks at Reedy (Report 102R) are indistinguishable on their Ti/Zr ratios but, in the main, the ultramafic rocks are richer in Cr than the mafic. In spite of this, there are some ultramafics at Reedy with low Cr. Although Cr abundances are high throughout most of the regolith derived from ultramafic rocks at Mt. Percy, there is strong depletion of Cr in the overlying lateritic duricrust and lateritic gravels. This is apparently due to loss of Cr, which is here hosted by weatherable chlorite rather than resistant chromite.

Multi-element discriminant analysis

This technique attempts to maximize the differences between pre-determined groups. It is essential to supply well-controlled data and to assess the results with care. This technique has been used at Reedy (Report 102R) to distinguish between the five major rock groups, namely ultramafic, mafic and mica schists, black shales and porphyries. It is limited by a number of assumptions that may be met only in part by the geochemical data. It is assumed that the data have a normal distribution, but this is seldom true, so that log or power transformations may have to be applied. The data should have no extreme values, which again is seldom the case. All known ore-related elements were eliminated from the analysis of the data from Reedy to attempt to meet this criterion. The data should not sum to a constant value, consequently major elements should be excluded and only minor and trace elements used. The number of samples in each 'training group' should exceed the number of elements by a factor of at least three and preferably by ten. It was not possible to meet this requirement for the smaller groups in the Reedy data.

Despite these limitations, the results from Reedy were better than expected. The best results were achieved using power transformation (though log transformation was fairly satisfactory) and a group of 7 elements, Cr, Nb, Co, Sc, Lu, Hf and Ba (Figure 3.3). This resulted in 91% correct classification. Log transformation and a smaller set of four elements (Cr, Sc, Co and K) resulted in 85% success. In these procedures, the first few elements do most of the discrimination and the stepwise addition of more elements makes a progressively smaller improvement. The technique can be further improved by plotting the first two canonical variates and drawing curved boundaries between the fields.

There is still some misclassification and this could be due to:- (i) inaccurate analyses (thought to be insignificant), (ii) misidentification (possible, when considering the highly weathered state of the rocks) or (iii) hybrid compositions, due to the outward movement of elements from the ore shoots and porphyry bodies into their contact rocks. All in all the results were good, despite the variable and, in places, considerable state of weathering. At this stage these results can only be applied locally. Study of a greatly enlarged data set will be attempted in the continuation project P241A, in which it is hoped to define a group or a number of groups of elements that are most effective in rock discrimination.

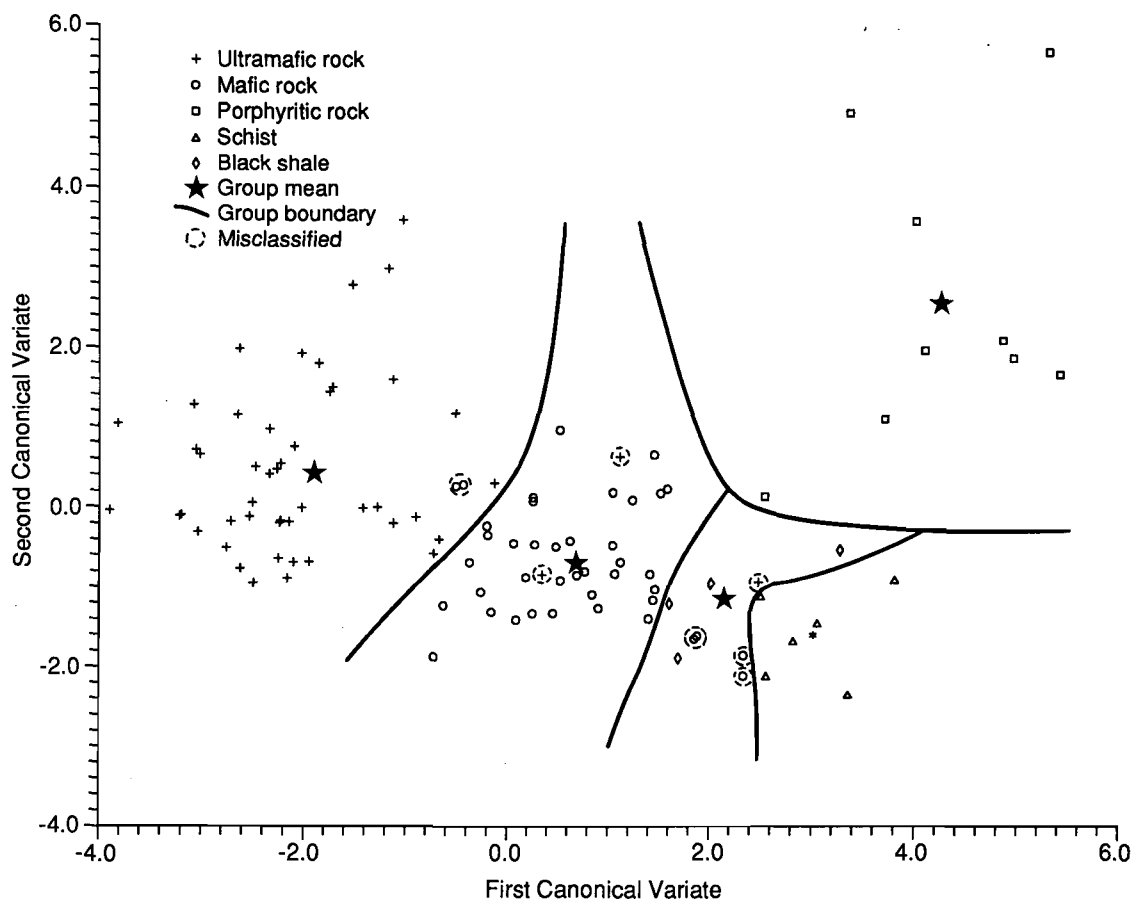


Fig 3.3 Canonical variate plots using power-transformed data, with curved boundaries between rock type groups.

4.0 GEOCHEMICAL DISPERSION IN THE DEEP REGOLITH

4.1 INTRODUCTION

Several investigations in the Project have determined the lateral and vertical distributions of gold and a wide range of other elements in the regolith close to mineralization. The principal objective has been to establish which elements may indicate or confirm the presence of mineralization where gold itself has been leached (e.g., from near-surface depletion zones) or has a restricted or irregular distribution (e.g., within saprolite). The data are also relevant to studies of the genesis of supergene gold deposits and to the evolution of the regolith.

The sites investigated in most detail are Mt. Percy (Report 156R), Beasley Creek (Report 152R) and Reedy (Report 102R), which were sampled as follows:

1. Duplicates of grade-control samples: Mt. Percy.
2. Spot samples from the pit wall: Reedy
3. Drill fence: Beasley Creek.

Additional information was obtained from Callion, Panglo, Bottle Creek, Mt. Magnet and Telfer, mainly from percussion and diamond drilled samples, supplemented by specific spot and channel samples. Grade-control duplicates give the most satisfactory sample density, and sampling programmes were commenced at other sites; unfortunately, operational problems interfered and sampling was abandoned. (Equivalent studies based on grade-control sample duplicates have been undertaken at Hannan South and Mt. Pleasant in a separate project (Lawrance, PhD thesis in preparation) but the data cannot yet be released). Selected data are summarized on Figures 4.1 to 4.6.

4.2 GEOLOGY, GEOMORPHOLOGY AND PRIMARY GEOCHEMISTRY

Some characteristics of the principal sites are summarized in Table 4.1. From an exploration viewpoint, the essential features are:

1. The geomorphology of the site, including the degree of preservation of the regolith profile. This indicates the nature and origin of the sample material and the size and type of anomaly that might be found. It is particularly important to determine whether the lateritic horizon is present, even if buried, for this tends to give broader anomalies and higher concentrations of many elements compared to underlying horizons.
2. Element associations and abundances in the mineralization. These indicate which elements have most potential as pathfinders. In summary, As, Ag, Sb and W accompany Au mineralization at each site, in varying abundances. Copper, Pb, Zn, Mo, Bi and Sn occur sporadically, perhaps regionally associated with sulphide mineralization; Te and B are present in specific deposit types (e.g., Mt. Percy and Mt. Magnet respectively). In general, the low abundances of Ag, Bi, Sn and Te reduce their potential as pathfinders. Increased abundances of K and Rb reflect the muscovite (or fuchsite) in the alteration zones around several deposits, but are also high in micaceous unmineralized rocks. Similarly, although most deposits are enriched in Ba, higher concentrations are present in rocks such as felsic porphyries and so may be unrelated to mineralization.

Table 4.1 Geochemical dispersion sites: summarized geology and geomorphology.

	MYSTERY PIT, MT. PERCY		BEASLEY CREEK	RAND PIT, REEDY
Geological setting	E-dipping limb of Kalgoorlie Anticline, 6 km N of Golden Mile. Chlorite talc carbonate rocks (Hannan's Lake Serpentinite) intruded by felsic porphyries.		Black shales within mafic amphibolite schists and komatiites of the Mt. Margaret anticline.	Mafic and ultramafic schists, carbonaceous mica schists and felsic porphyries in Mt. Magnet-Meekatharra greenstone belt.
Mineralization	Within porphyries and adjacent fuchsite alteration zones in the ultramafic rocks. Pyritic, some quartz veining; free Au (> 20% Ag), Ag-Au tellurides.		Pyritic black shales, some K-mica alteration. Nature of fresh mineralization unknown.	Pyritic biotite quartz chlorite feldspar schist with fuchsite carbonate alteration. Free gold (<15% Ag; some very coarse), auriferous pyrite.
Primary geochemistry	Ore	Background	Ore Background (Partly weathered)	Ore Background
> 0.5 %	K		Mn	K
1000-5000 ppm	S		Mn	
500-1000 ppm		K		K
100-500 ppm	Ba		As Ba Cu	Cu Ba Zn
50-100 ppm		S	Co Co	Rb Cu Zn
10-50 ppm	As W Rb	Ba	Ce La Rb Y	As Pb W Ba
1-10 ppm	Au Ag Te Sb	Rb	Au W	Au Bi Cd Mo Rb
	Pb			Se Sn
<1 ppm		Au Ag As Pb Sb W Te	Ag Bi Cd Sb Au Ag As Bi Ce La Pb Sb W	Ag Sb Au Ag As Bi Cd Mo Pb Sb Se Sn W
Geomorphological setting	Crest, upper slope. Possible inverted topography.		Low rise of exposed residuum in plain of Permian and alluvial sediments.	Erosional plain, mid-slope, low gradient.
Regolith	Complete lateritic profile, some erosion of lateritic gravels. Profile 60-70 m thick.		Mostly truncated to upper saprolite, some remnant lateritic duricrusts and gravels. Profile 40-50 m thick; > 200 m over mineralization.	Profile mostly truncated to lower mottled zone. Lateritic remnants thicker to N and S. Profile 50-60 m thick.
Surface	Calcareous gravelly earths; cuirasse outcrop on talc chlorite rocks.		Thin soils, some calcrete, hardpan and outcrop.	Acid sandy clay loam over thin hardpan (silicified colluvium); some lateritic gravels.

TABLE 4.1 (continued)

	GLASSON DEPOSIT, CALLION		PARKINSON PIT, MT. MAGNET		PANGLO	
Geological setting	E-dipping metabasalts, interflow metasediments and felsic metatuffs in the Davyhurst-Mt. Ida greenstone belt.		Foliated mafic and felsic volcanic rocks and minor cherts in the Mt. Magnet-Meekatharra greenstone belt.		Mafic and ultramafic volcanic rocks, quartz-chlorite-muscovite-carbonate shales.	
Mineralization	Quartz veins in shear zone between fine and medium grained metabasalts, sub-parallel to the stratigraphy. Free gold and disseminated sulphides.		Steeply dipping, discontinuous pyrite and quartz-tourmaline-pyrite lodes.		Pyritic quartz shear zones. Mineralization mainly supergene with primary source poorly defined.	
Primary geochemistry	Ore	Background	Ore	Background	Ore	Background
> 0.5 %	K		K S		K	K
1000-5000 ppm	Cr	K		K	S	S
500-1000 ppm				S		
100-500 ppm	As Cu Zn	Cr	B Ba	Ba	As Ba Cu	
50-100 ppm	Ba Cu Rb	Zn	As	As B	B Pb Zn	As Ba Cu Pb
10-50 ppm	B W	Ba	W Rb		Sb Rb W	B Rb Zn
1-10 ppm	Au Ag	B Rb As	Au	W	Au Mo Sn	Mo Sb Sn
< 1 ppm		Au Ag	Ag	Au Ag	Ag	Ag Au W
Geomorphological setting	Low residual lateritic hills.		Gently sloping erosional surface, slightly elevated.		S flowing saline drainage marginal to playa. Water-table at 5 m.	
Regolith	Complete lateritic profile with strong calcrete development in the ferruginous horizon. Profile 60-70 m thick.		Truncated in leached upper saprolite. Profile 35-60 m thick.		Truncated to clay-rich upper saprolite. Profile commonly > 50 m thick.	
Surface	Lateritic gravels and calcareous gravelly soils.		Red brown silty loam, calcareous and locally gypsiferous.		Sandy red earths, saline and/or gypsiferous and/or calcareous. Commonly part-transported, on saprolite.	

4.3 REGOLITH GEOCHEMISTRY

4.3.1 Gold

The observed distributions of Au are similar to those previously reported in the literature. The principal features are:

1. 'Lateritic' enrichment

Where the profile is complete, or nearly so, there is a widespread zone of Au enrichment close to the surface, within lateritic duricrust and gravels and in overlying residual soil. This is particularly well developed at Mt. Percy and Callion, and was also observed at Mulline, Bardoc and Reedy, the enrichments being mineable as 'lateritic ore'. Except at Reedy, however, a considerable proportion of the Au is associated with pedogenic carbonates, rather than solely with the Fe oxide phases. Where the lateritic horizon has largely been eroded, as at Beasley Creek and Reedy (Rand pit), remnant gravels retain the enrichment as an anomaly detectable by lag sampling although, at these sites, Au is not sufficiently abundant to mine; there is little carbonate and the Au is associated mainly with the Fe oxides. (NB. Other pits at Reedy were mined for lateritic ore and exhibited similar enrichments to those at Mt. Percy and Callion). At Panglo and Mt. Magnet, the profiles have been truncated so that any former lateritic enrichment has been removed.

2. Depleted zone

A leached and depleted zone (<100 ppb Au) is present in the upper, clay-rich zones of the regolith developed over primary mineralization. This is most evident at Mt. Percy as a 5-10 m thick zone beneath the ferruginous horizon, and at Mt. Magnet and Panglo where the depleted zone now subcrops beneath the soil. Depletion is less evident at Callion and Reedy, possibly due to Au preserved within quartz, and is not observed over the main ore zone at Beasley Creek. (A depletion zone 20 m thick is present in the highly saline regolith at Hannan South (Lawrance, 1991), and is also reported from Bardoc. Such depletion is an important feature of the regolith over most weathered Au mineralization in Western Australia where the profile is relatively complete).

3. Supergene enrichment

This has occurred within part of the saprolite over the primary mineralization and wallrocks at Mt. Percy and Panglo; it is not apparent at Beasley Creek, Reedy and Callion, but the data are insufficient to be conclusive. However, enrichment at Callion was reported by Glasson *et al.*, (1988). Nevertheless, at each site studied, most Au in the saprolite is secondary, indicating that remobilization and homogenization of the Au distribution has occurred. Dispersion and enrichment at Panglo is particularly important, forming an extensive sub-horizontal zone at 30-40 m depth. This enrichment zone is similar to that at Hannan South, also beneath the water-table in a highly saline environment.

4.3.2 Elements associated with mineralization: S, Ag, Te, As, Sb, W, Tl, B, Ba, K, Rb

Each of these elements behaves differently during weathering and none has a distribution similar to that of Au. *Sulphides* are generally the minerals most susceptible to weathering and S is leached deep in the regolith except where it is present in barite. There is some secondary concentration of S in alunite in the upper saprolite at Mt. Percy and Panglo, and in gypsum in soils at several sites, notably Beasley Creek. The exploration significance of these secondary S minerals is not certain. *Silver* and *Te* are also generally strongly leached and abundances are commonly too low for dispersion patterns to be detected. However, Ag appears to be retained through much of the profile at Beasley Creek (0.5-1 ppm), possibly with some depletion in the upper saprolite, but with dispersion into the overlying mottled zone and duricrust in the hanging wall. Secondary Ag halides are present in the lower saprolite at Mt. Percy. *Arsenic* becomes more homogeneously distributed and concentrated by weathering, being retained throughout the regolith, except in the clay saprolite at Mt. Percy and possibly Reedy. It concentrates particularly with Fe oxides and is laterally dispersed at the surface with lateritic gravels, duricrusts and lags. Very high concentrations (>5000 ppm As) are present in some saprolites and gossans at Telfer. *Antimony* and *W* are both retained and generally residually concentrated

within the regolith over the mineralization and alteration zones, with anomalies extending into barren wall rocks high in the profile. Antimony, W and, to a lesser extent, As, are retained through the depleted zone and hence have potential importance in exploring areas where leaching is extreme. Antimony and W are more specific to Au mineralization, but abundances may be low (e.g., Sb at Reedy and Telfer) and there is potential for W contamination during drilling and sample preparation. Tungsten is particularly abundant at Telfer (100- >1000 ppm) and gives a homogeneous anomaly at Mt. Percy (5-40 ppm). Arsenic is less specific but its greater mobility during weathering results in a more widespread dispersion halo; there is, however, the possibility of spurious secondary concentration.

Thallium was determined only at Reedy, where it seems to discriminate both ore and porphyry pods, with some lateral dispersion in the top 5 m of the regolith. *Boron* is associated with mineralization at Reedy and Mt. Magnet, where it occurs in tourmaline, but is also widely dispersed at 10-40 ppm in the clay-rich upper saprolite. Similar enrichment and dispersion is seen at Callion (>100 ppm), Mt. Magnet (>70 ppm) and Panglo (20-40 ppm). It is possible that this association is related to the occurrence of the clays, rather than the presence of mineralization.

Barium, *K* and *Rb* are commonly, but not exclusively, associated with Au mineralization or the alteration zone. Each is hosted by resistant minerals (secondary barite (Ba) and primary muscovite (Ba, K, Rb)) that persist through the regolith, only being partly destroyed in the ferruginous horizon. They may thus present a geochemical and mineralogical indication of the primary mineralized system, even within the depleted zone. At Beasley Creek, increased Rb contents, with minor Au, As and Ba, in the lower saprolite about 150 m W of the main orebody may represent alteration associated with further mineralization. In contrast, K and Rb hosted by weatherable minerals such as biotite and feldspar are leached deep in the profile. Some K occurs with S in alunite.

4.3.3 Major elements: Fe, Si, Al

These elements are commonly the principal residual products of deep weathering, occurring as the oxides (e.g., goethite, hematite, gibbsite, quartz, hyalite) or as aluminosilicates (kaolinite, halloysite, allophane). Each is enriched in the lower to mid-saprolite, commonly by factors of 2 or more, due to residual concentration following the leaching of other components such as Ca, Mg and Na. Remobilization and further concentration take place in some upper horizons and obscure differences between lithologies. *Iron* is strongly enriched towards the top of the profile, appearing in the upper saprolite as diffuse stains of secondary Fe oxides and subsequently as discrete segregations such as nodules, pisoliths and vein- and void- coatings that concentrate in the mottled and ferruginous horizons. *Silicon* and *Al* become most strongly enriched towards the top of the saprolite, but are depleted above as aluminosilicates (and quartz) are replaced by Fe oxides. Over Al-poor ultramafic rocks, Si is concentrated as silcrete, but over other lithologies, the upper saprolite is dominantly kaolinitic, possibly with an absolute increase in Al content (e.g., above the chlorite talc carbonates of the Hannan's Lake serpentinite at Mt. Percy). The Al is probably derived from the replacement of clays during the formation of the overlying ferruginous horizon; some Al is retained within hematite and goethite so that some duricrusts and gravels, e.g., at Beasley Creek, are relatively enriched in Al compared to most underlying horizons of the regolith.

4.3.4 Alkaline earth elements: Mg, Ca, Sr, Ba

Magnesium, Ca and Sr have many similarities in their distribution in the regolith. They are strongly leached at the onset of weathering, particularly where they occur dominantly as carbonates, and are almost totally depleted from some upper horizons. They may, however, be re-concentrated at or close to the surface in pedogenic calcrete. Barium behaves somewhat differently, being relatively enriched through most of the regolith, possibly being leached only very close to the surface; it reprecipitates as the insoluble sulphate (barite) rather than as a carbonate and so does not occur solely with the carbonates in the calcrete-bearing horizons. *Magnesium* is commonly more persistent than Ca and Sr in the saprolite due to the relative resistance of ferromagnesian minerals (e.g., chlorite and, particularly, talc) and the precipitation of secondary magnesite over some ultramafic rocks. *Calcium* and *Sr* are both leached more strongly than Mg, but their

relative behaviour is dependent upon their primary host minerals. Both tend to be more strongly enriched and closely correlated in the surface, probably because Sr substitutes for Ca in pedogenic carbonate minerals.

The distributions of Ca and Sr at Mt. Percy (Report 156R, Appendices I and II) and Panglo (See Figures 4.1 and 4.4) are characteristic of semi-arid parts of the Yilgarn Block south of the Menzies Line (Report 156R, Appendices I and II). They have particular significance given the association between carbonate alteration and mineralization in many Archaean Au deposits and the enrichment of gold in horizons containing pedogenic carbonate. North of the Menzies Line (Figure 1, p. iii), a similar distribution is present at Mt. Magnet, although pedogenic carbonate is regionally less significant (Report 178R, Figure 13). Magnesium, Ca and Sr are less strongly leached at Reedy and, in particular, Beasley Creek, due to a greater initial abundance of ferromagnesian minerals than carbonates. Pedogenic carbonate is absent at Reedy and is only patchily developed at Beasley Creek, although here some carbonate accumulation also occurs at the top of the saprolite (Report 152R, Appendix 5).

4.3.5 Base and transition metals: Cu, Zn, Pb, Mn, Co, Ni

These are considered together because the base metals (Pb, Zn, Cu) are associated with some primary Au mineralization and because the transition metals (Mn, Co, Ni, Cu and Zn) have many similarities in chemical behaviour in the weathering environment. Nevertheless, there is no consistent enrichment of base metals with the primary Au mineralization at any of the sites studied except Telfer and Bottle Creek, although secondary Cu minerals are locally prominent at Panglo. Pyrite is the most abundant sulphide mineral and only a few grains of other sulphides (e.g., galena, chalcopyrite, sphalerite, arsenopyrite, millerite, pyrrhotite, pentlandite, cobaltite, gersdorffite) have been recorded during these studies. The situation at Beasley Creek is a little different, with concentrations of these elements in the mineralized shale, particularly of Mn, being much higher than the wall rocks and showing little redistribution in the regolith. Telfer is a more sulphide- and base metal-rich deposit and has locally high concentrations of Cu and Pb, particularly in the gossans (Report 187R, Table 3).

The distribution patterns of *Mn*, *Co*, *Ni*, *Zn* and, in part, *Cu* have a number of similarities. All are leached from the upper horizons of the regolith (ferruginous zone to upper saprolite) and are patchily enriched, together or separately, at depth. Unlike the other elements, the overall Mn content of the regolith is much lower than that of the parent material. Similarities between the distributions of Mn and Mg deep in the profile imply that these metals are hosted by the same primary minerals, i.e., ferromagnesian minerals and dolomite, and are released together on weathering. There is a sharp decrease in Mn content at the base of the saprolite, probably due to the weathering of dolomite; the other transition metals are weakly enriched, a concomitant residual effect. In the remainder of the regolith, the Mn distribution is very similar to those of Co, Ni and Zn, which also have ferromagnesian minerals as the dominant primary hosts. The weak surface enrichment of Cu at Reedy is unusual, and is possibly dispersed from the mafic units. There is no evidence for Cu enrichment in lateritic or mottled horizons over ultramafic rocks similar to that observed at Mt. Keith (Butt and Nickel, 1981), nor for substantial Ni, Co or Mn concentrations of the "lateritic nickel" type.

The abundance of Pb is mostly low, with a few sporadic high values, and it has a distribution similar to that of immobile elements such as Zr. The Pb abundance is rather greater at Beasley Creek and a narrow zone of high values (100-150 ppm) in surficial mottled and clay zones extends laterally for over 400 m down slope to the west. This dispersion halo is reminiscent of that reported at Teutonic Bore (Greig, 1983), although this was at 20 m depth. In gossans (e.g., Bottle Creek, Report 36R), high concentrations of Ag, As, Ba, Cu, Pb, Sb and Zn are due to their retention in alunite/jarosite minerals.

4.3.6 Lithophile transition elements: Sc, Ti, V, Cr

These elements commonly accumulate in lateritic regoliths, particularly in the ferruginous horizons. The host minerals for these elements are commonly secondary Fe oxides (Cr, V, Sc) and anatase (Ti) and resistant chromite (Cr) and rutile (Ti). Each is generally concentrated twofold or more in the saprolite and clay-rich horizons and further concentrated in the overlying duricrusts and gravels. The concentrations are largely residual, being due to the loss of other components. At Mt. Percy, however, although this appears true of Ti and V, the distribution of Cr is unusual in that it is concentrated with kaolinite in the upper, clay-rich saprolite, the plasmic horizon and mottled clay zone and is at anomalously low concentrations in the lateritic duricrust and gravels. The Sc distribution is similar to that of Cr, although it is also reduced where the upper horizons are silicified. These data demonstrate how the Cr distribution in lateritic regoliths is strongly influenced by its primary host mineral. In many ultramafic rocks, most Cr is hosted by chromite, which is generally resistant to weathering. Chromium thus tends to accumulate in the duricrust, commonly to 1.0-5.0% (e.g., Smith, 1977). At Mt. Percy, however, chromite is uncommon and most Cr is present in ferromagnesian minerals, principally chlorite, with some in fuchsite (chromian muscovite) in the alteration zone. In the upper saprolite, chlorite is weathered to kaolinite which, in turn, is replaced by Fe oxides in the lateritic horizons. The Cr in chlorite is apparently incorporated in kaolinite, colouring it green; together with Al, it is released again when the kaolinite is destroyed and reincorporated in neo-formed kaolinite and Fe oxides in the underlying horizons. The mottled and clay zones thus become Cr-rich (0.8-1.0%), compared to <700 ppm in the cuirasse.

Titanium is particularly strongly concentrated (>2%, locally >10%) in the massive duricrust (cuirasse) over the talc chlorite carbonate rocks at Mt. Percy. It is probably in part dispersed laterally from the adjacent porphyries, which have an initially higher Ti content. In comparison, V is particularly abundant in the host shale at Beasley Creek (500-800 ppm), reaching 1000-2000 ppm in the mottled zone and duricrust over the hanging wall. The distribution suggests that the host unit would previously have been indicated by a strong V enrichment in the ferruginous zone, now largely dismantled by erosion. Although roscoelite (vanadian muscovite) is present in one sample at Mt. Percy, there is no association between the distributions of V and Au mineralization.

4.3.7 Immobile elements: Zr, Hf, Th, Nb, Ta

These elements generally exhibit little chemical mobility in the weathering environment and follow this behaviour at each of the sites studied, although minor *Th* mobility is apparent at Panglo (Report 41R). Their abundances increase upwards through the regolith and all five elements are enriched in the lateritic duricrusts and gravels, where present. Residual concentration and physical transport in these horizons has led to wide dispersion at Mt. Percy and Beasley Creek. The resistance of Zr to weathering gives it great value for distinguishing different lithologies in the regolith, except in these upper, partly transported and mixed units (see Section 3.5.4).

4.3.8 Rare earth elements: Y, La, Ce, Sm, Eu, Yb, Lu

The distributions of these elements have a number of general characteristics in common, with some variations corresponding to whether they are "light" (*La, Ce, Sm*) or "heavy" (*Eu, Yb, Lu and Y*). These variations probably relate to the relative resistance to weathering of primary host minerals having different REE signatures. Discrimination between lithologies on the basis of REE abundances is maintained in the lower saprolite, but the light REE in particular are strongly depleted in the upper saprolite and clay-rich horizons. This depletion continues to the surface at Reedy and Beasley Creek, but at Mt. Percy, where the lateritic profile is essentially complete, there is some concentration of the REE in the lateritic duricrusts and gravels. Nevertheless, this concentration is greater for the heavier elements Y, Yb and Lu, particularly in the massive duricrust (cuirasse) over the talc chlorite ultramafic rocks. Lateral dispersion and enrichment of REE is possible at Reedy.

An important feature of the distributions of all REE at Mt. Percy is an enrichment in the lower saprolite, at a level corresponding to an increase in hardness and porosity. The maximum enrichments (e.g., 80-110 ppm La, 80-130 ppm Ce, 10-22 ppm Sm and 2-5 ppm Eu) occur in the weathered porphyries but extends laterally into the weathered ultramafic wallrocks.

The ore host rocks at Beasley Creek and, in particular, Telfer are indicated by high concentrations of La and Ce, which might constitute pathfinders for these units. However, there is no obvious relationship between REE and mineralization as such.

4.4 IMPLICATIONS FOR EXPLORATION

4.4.1 Introduction

The multi-element dispersion patterns revealed by these studies have several implications for Au exploration, as well as providing some ancillary data of relevance to exploration for other commodities. In general, the data support the contention that at local to sub-regional scales, Au itself is one of the best indicators of Au mineralization, despite (or perhaps because of) its chemical mobility during weathering. The principal proviso to this observation is that sampling must take account of the distribution of Au in the regolith; in particular, the accumulation of gold in calcareous and ferruginous surface horizons and its depletion for 5 to 20 m below them, implies that sampling has to be carefully directed and that data interpretation will depend on the horizon sampled. Other elements commonly provide confirmatory evidence for the presence of mineralization and have particular value when Au has been depleted, is patchily distributed or where samples have been derived from the alteration zone rather than from the mineralization itself. A possible example is the Au-As-Ba-Cd-Rb \pm Ag-Bi-Ge-Pb-Sn-W anomaly in the saprolite west of the mineralization at Beasley Creek; the association suggest this to be due to underlying primary mineralization, rather than to a secondary dispersion halo from the main deposit.

4.4.2 Lateritic materials and derived soils

Primary and supergene Au mineralization are indicated by broad Au anomalies in the lateritic duricrusts and the lags and soils derived from them. These anomalies are comprised of (i) primary and (mostly) secondary Au associated with Fe oxides and presumably accumulated during lateritic weathering and (ii) principally in the south of the Yilgarn Block, secondary Au associated with pedogenic carbonates and accumulated during recent arid phases. Mineralization is also indicated by high concentrations of other ore-associated elements in these surface horizons, principally W, As and, less commonly, Sb, but these do not appear to have wider or more consistent dispersion haloes than Au. Barium, K and Rb contents give a surface expression to the alteration zones, commonly wider targets than mineralization itself; K also offers potential for detection by radiometric surveys. However, these alkaline elements are not, of course, exclusively associated with mineralization.

4.4.3 Mottled and plasmic clay zones; upper saprolite

The "depleted zone" present over most Au deposits in the Yilgarn Block commonly occurs in these horizons. The location and thickness of the depleted zone varies, so that, in some deposits, one or more of these horizons may be depleted whereas, in others, they may even be enriched. Thus, at Mt. Percy, the Au content of the mottled zone is depleted and the upper (clay) saprolite is enriched, the opposite, for example, to the situation reported at Boddington (Davy and El Ansary, 1986). At sites where the regolith has been truncated and the ferruginous horizon is absent, the depleted zone commonly outcrops (Parkinson pit, Mt. Magnet), or subcrops beneath transported overburden (Panglo). The depleted zone is not always well developed (Callion, Beasley Creek) but its common occurrence demands that care must be taken to avoid sampling within it. The Au contents are generally <100 ppb, even where there are quartz veins, and give little or no indication of the

underlying mineralization. However, it is important to note that the other ore- and alteration-associated elements Sb, W, K, Ba and, to a lesser extent, As remain throughout the depleted zone; they would be expected to be anomalous in soils developed from depleted material in truncated regoliths even if Au contents are near to background values. If pedogenic carbonates are present, the depletion may be offset by some surface enrichment, as at Panglo and Mt. Magnet.

4.4.4 Saprolite

Gold in the saprolite beneath the depletion zone is generally present at abundances similar to those in the fresh rock. Lateral dispersion and concentration commonly occur at one or more levels, thereby enhancing the weathered expression of the primary mineralization and becoming an exploitable resource in its own right; much of this Au is secondary. Of the sites investigated, such concentration is best developed at Panglo where, as at Hannan South, recognition of the presence of an extensive, relatively thin horizon of Au enrichment is important for data interpretation and in devising exploration strategies for further such deposits. The abundances of the elements associated with Au mineralization are very variable, so that no universal 'threshold' values can be derived. Compared to the primary mineralization, element distributions (including Au) in the saprolite are more homogeneous, due to dispersion and reprecipitation during weathering. In general, dispersion and increase in size and coherence of secondary anomalies over primary distributions are:

$$S > Ag, Te \gg As > Sb > Au > W > Ba, K, Rb$$

Arsenic, Sb and W may give wider expression to mineralization in those saprolite zones in which Au has not been dispersed, whereas Ba, K and Rb indicate the broader target of the alteration zone. Silver, Te and S are very mobile and are generally leached to background values. However, at Mt. Percy and Panglo, S (and K) in alunite may be derived from the underlying mineralization, as may S in gypsum in soils at Beasley Creek. Also at Beasley Creek, Ag appears to be retained throughout the saprolite, indicating that although the mineralized unit is weathered to a considerable depth, it has not been very severely leached.

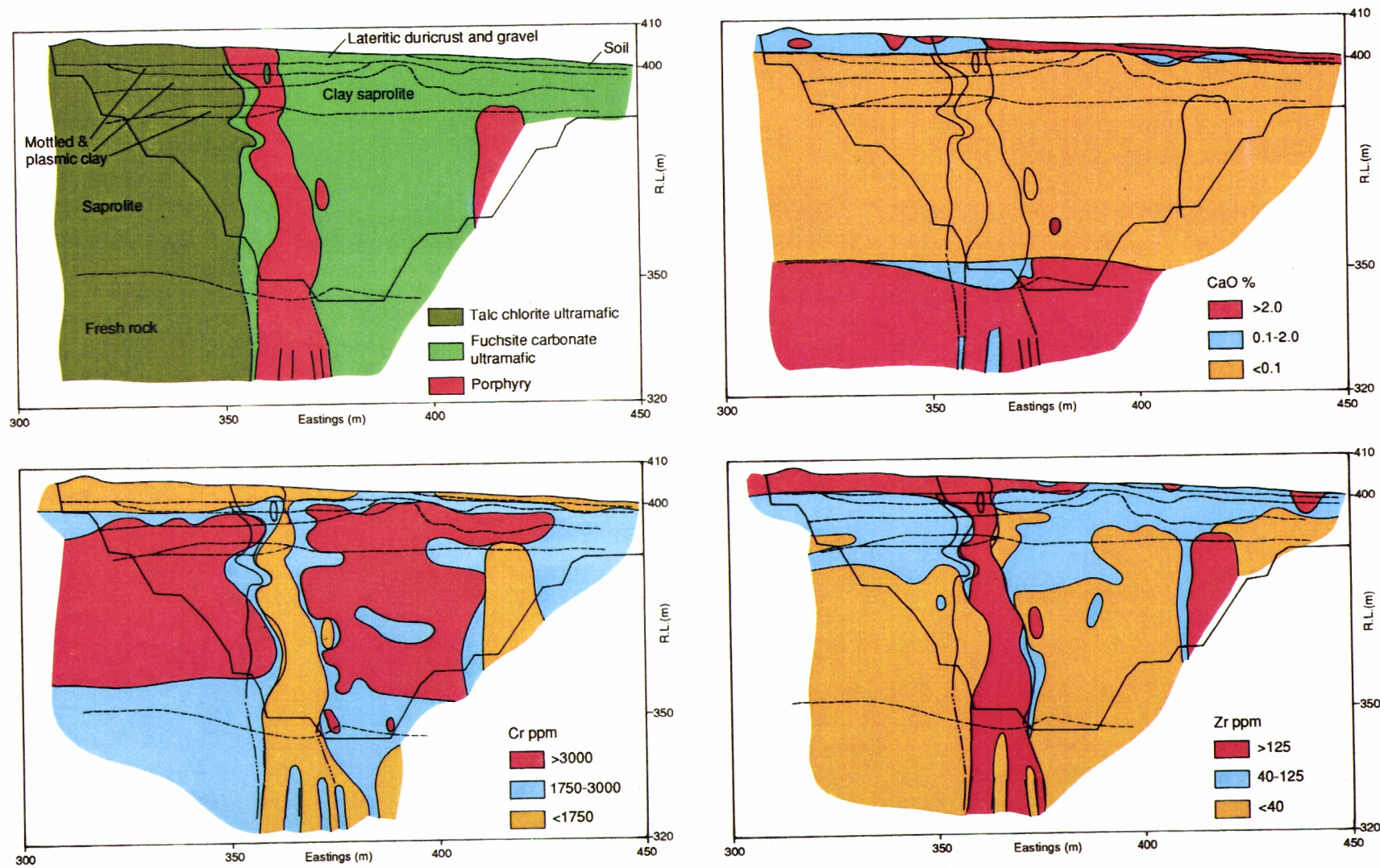
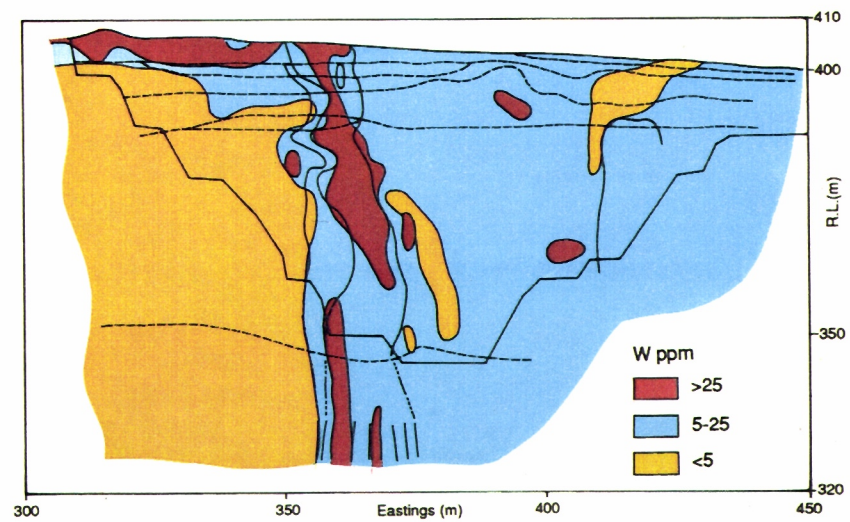
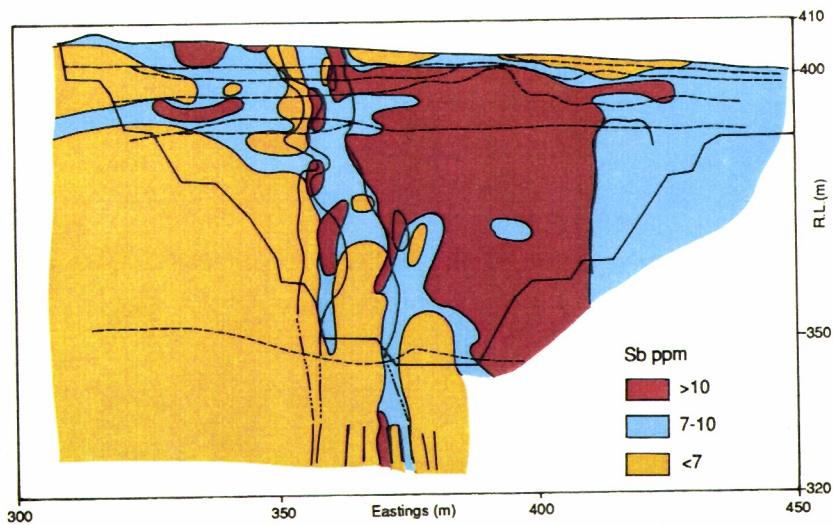
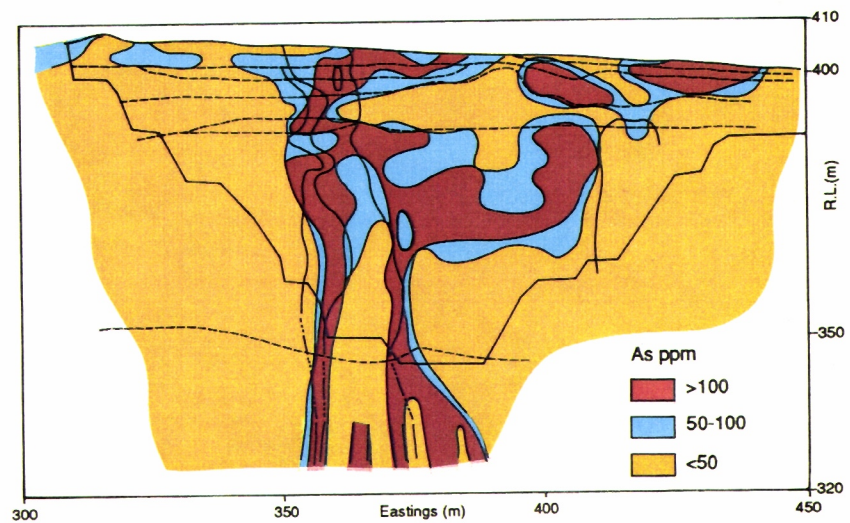
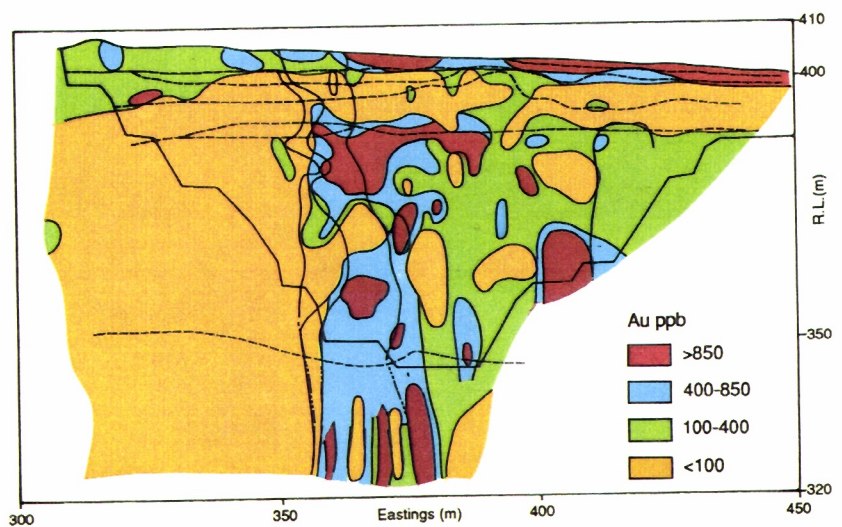


Figure 4.1

Regolith section, Mystery Zone, Mt. Percy (line 15850N).
Geology and distributions of CaO, Cr and Zr.

Figure 4.1 (continued) Regolith section, Mystery Zone, Mt. Percy (line 15850N). Au, As, Sb and W.



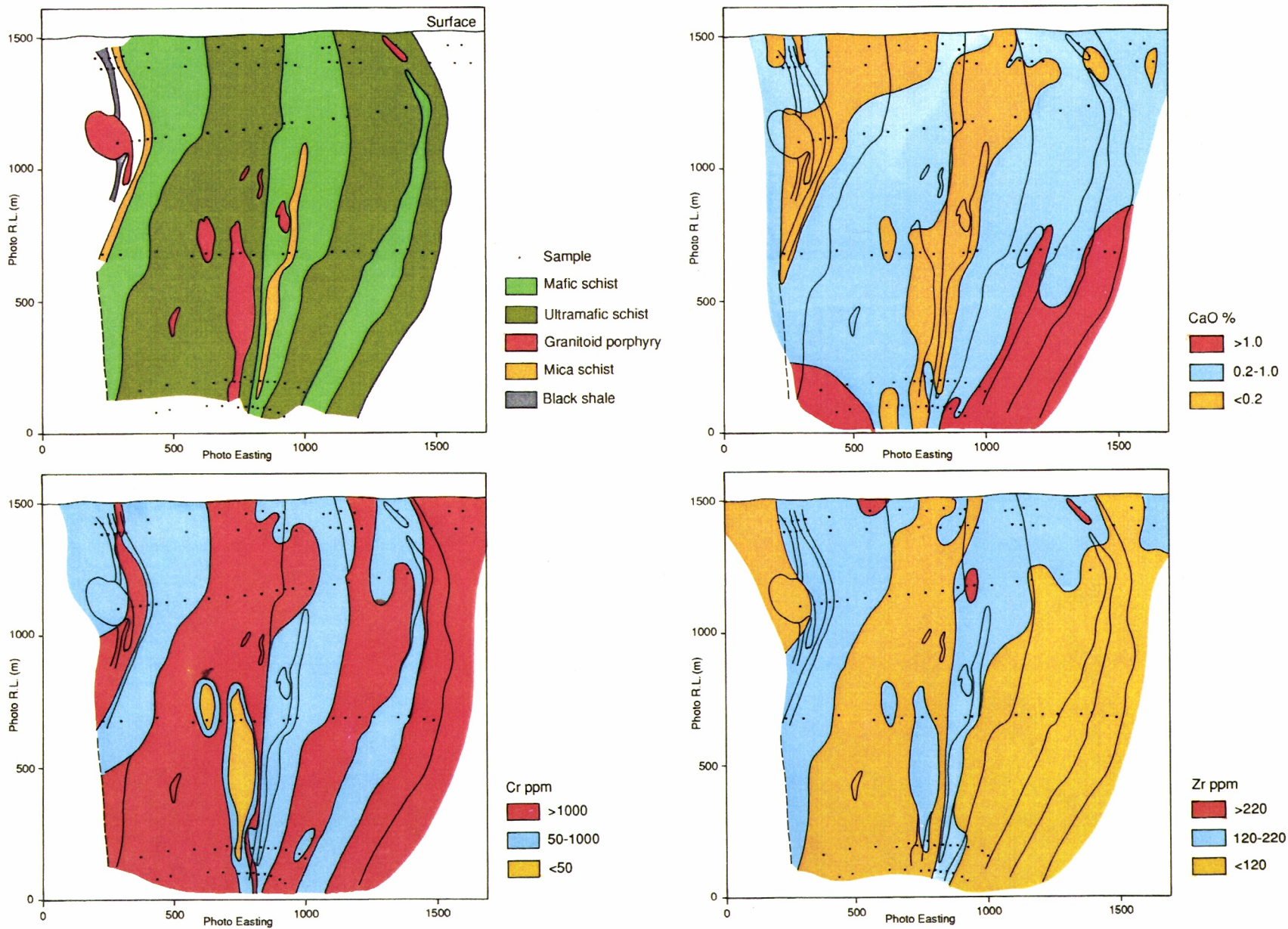
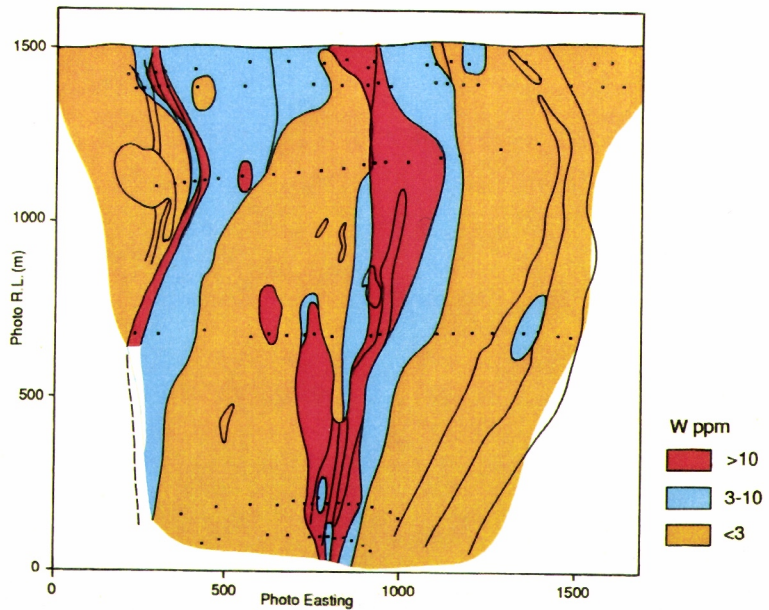
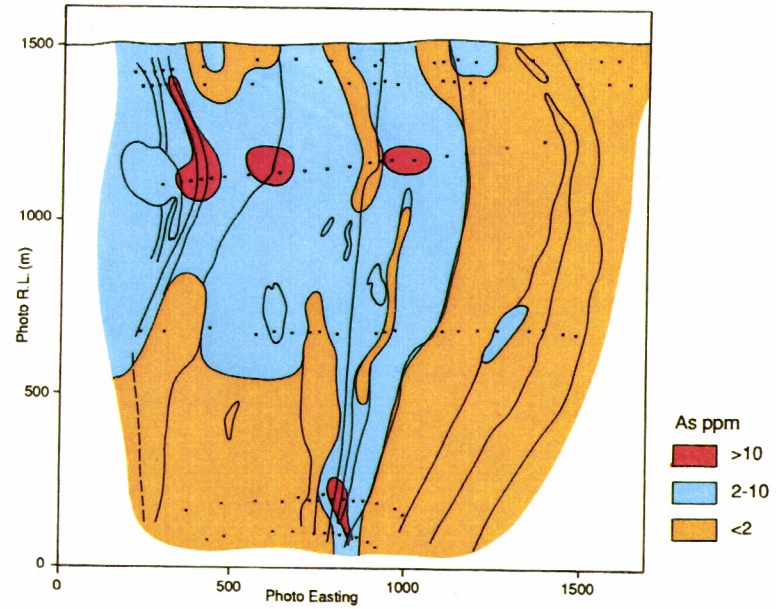
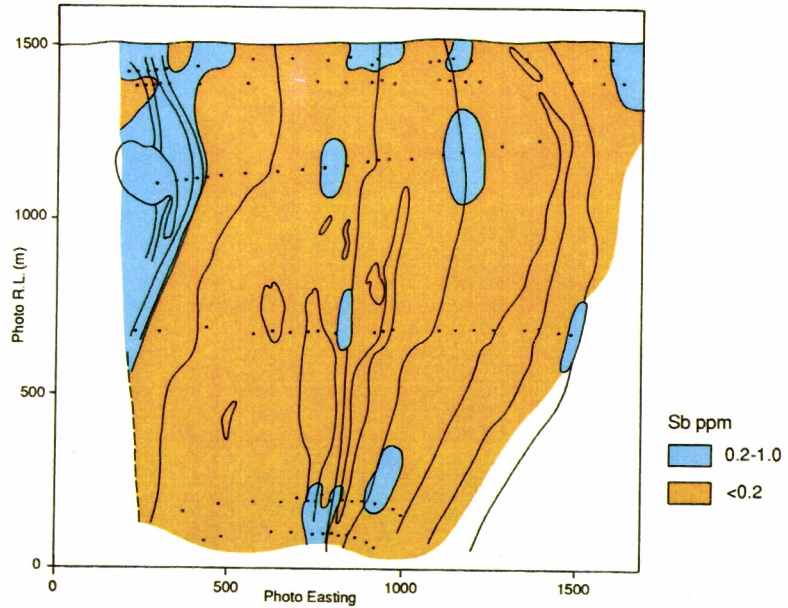
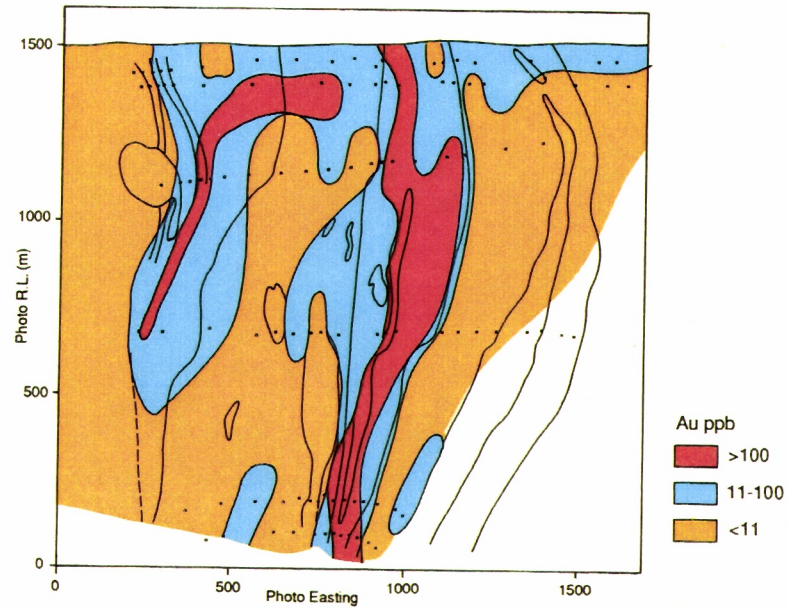


Figure 4.2 Regolith section, Rand Pit (south face), Reedy. Mostly saprolite; see Plate 3.1 Geology and distribution of CaO, Cr and Zr.

Figure 4.2 (continued) Regolith section, Rand Pit (south face), Reedy. Au, As, Sb and W.



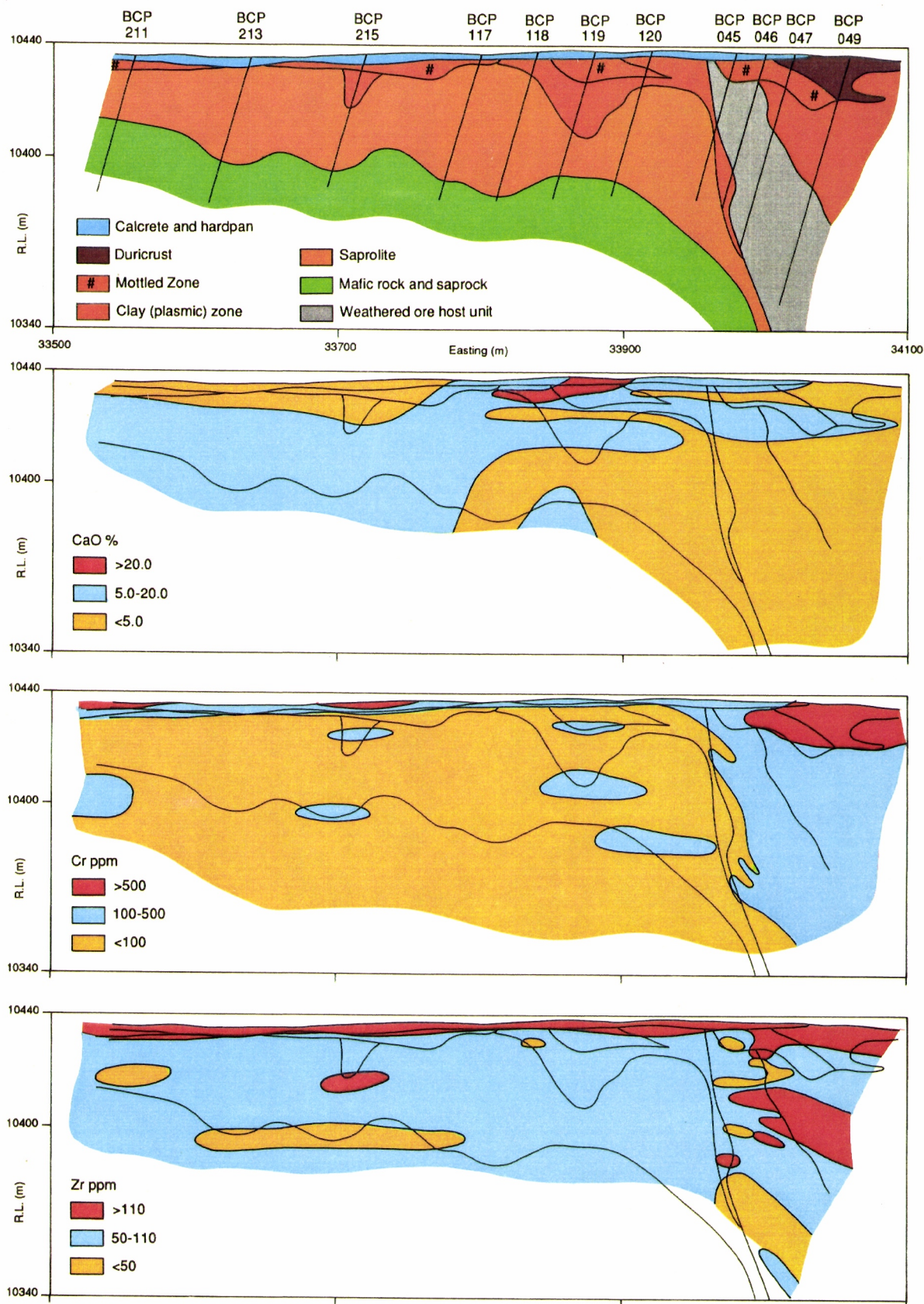


Figure 4.3 Regolith section, Beasley Creek (line 38820N). Geology and distribution of CaO, Cr and Zr.

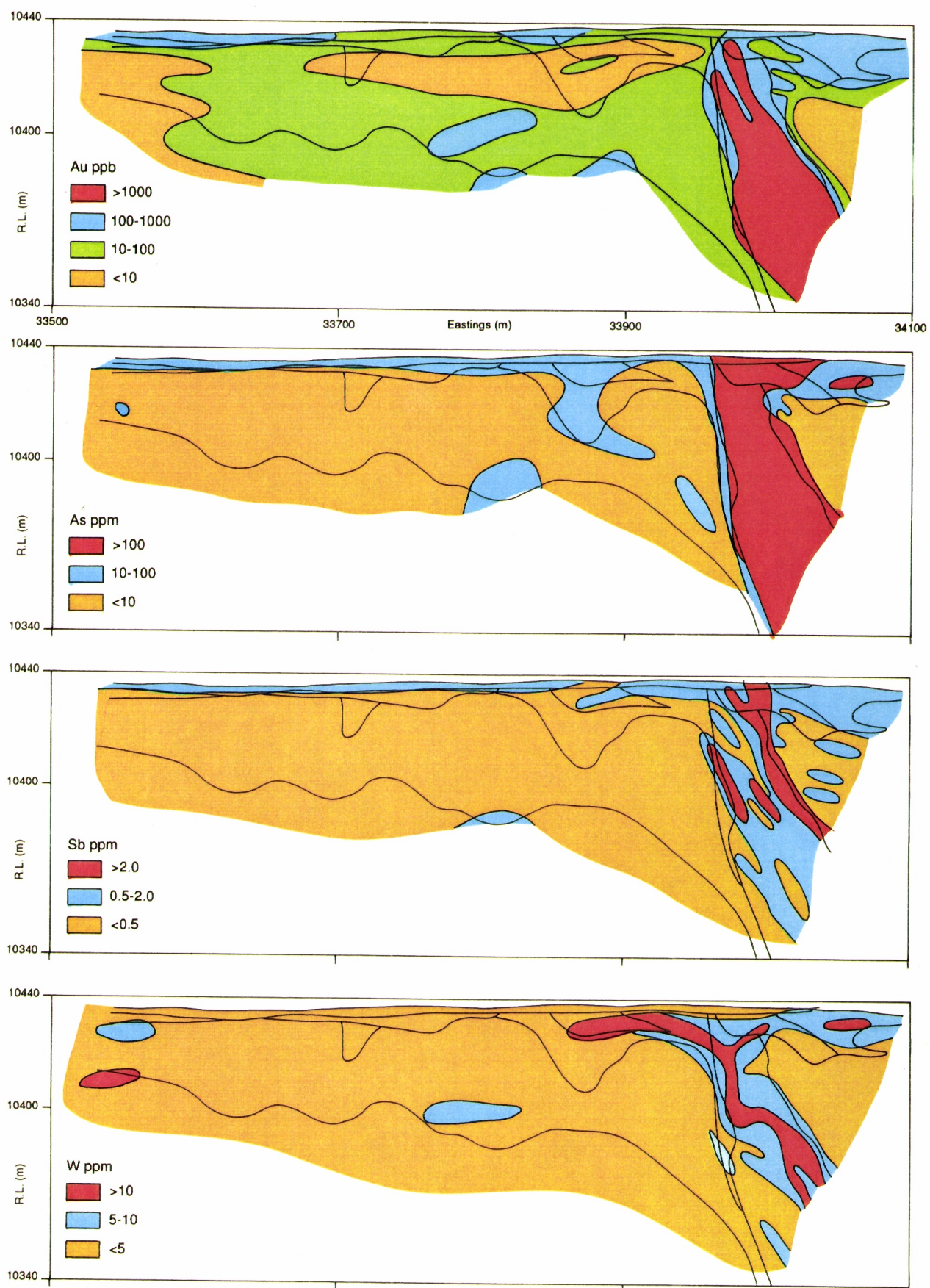


Figure 4.3 (continued) Regolith section, Beasley Creek (line 38820N). Au, As, Sb and W.

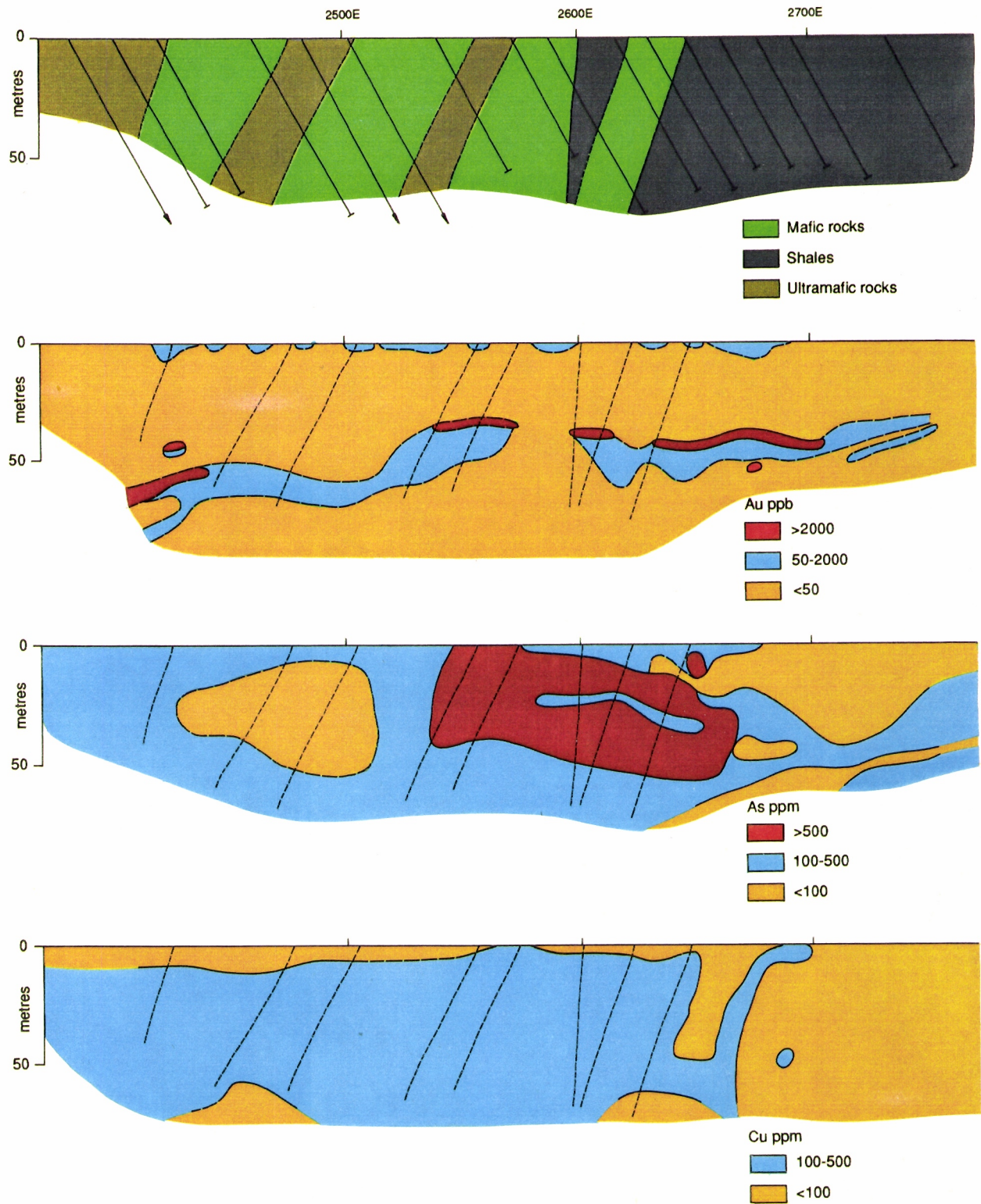


Figure 4.4 Regolith section, Panglo (line 4200N). Mostly saprolite. Geology and distributions of Au, As and Cu.

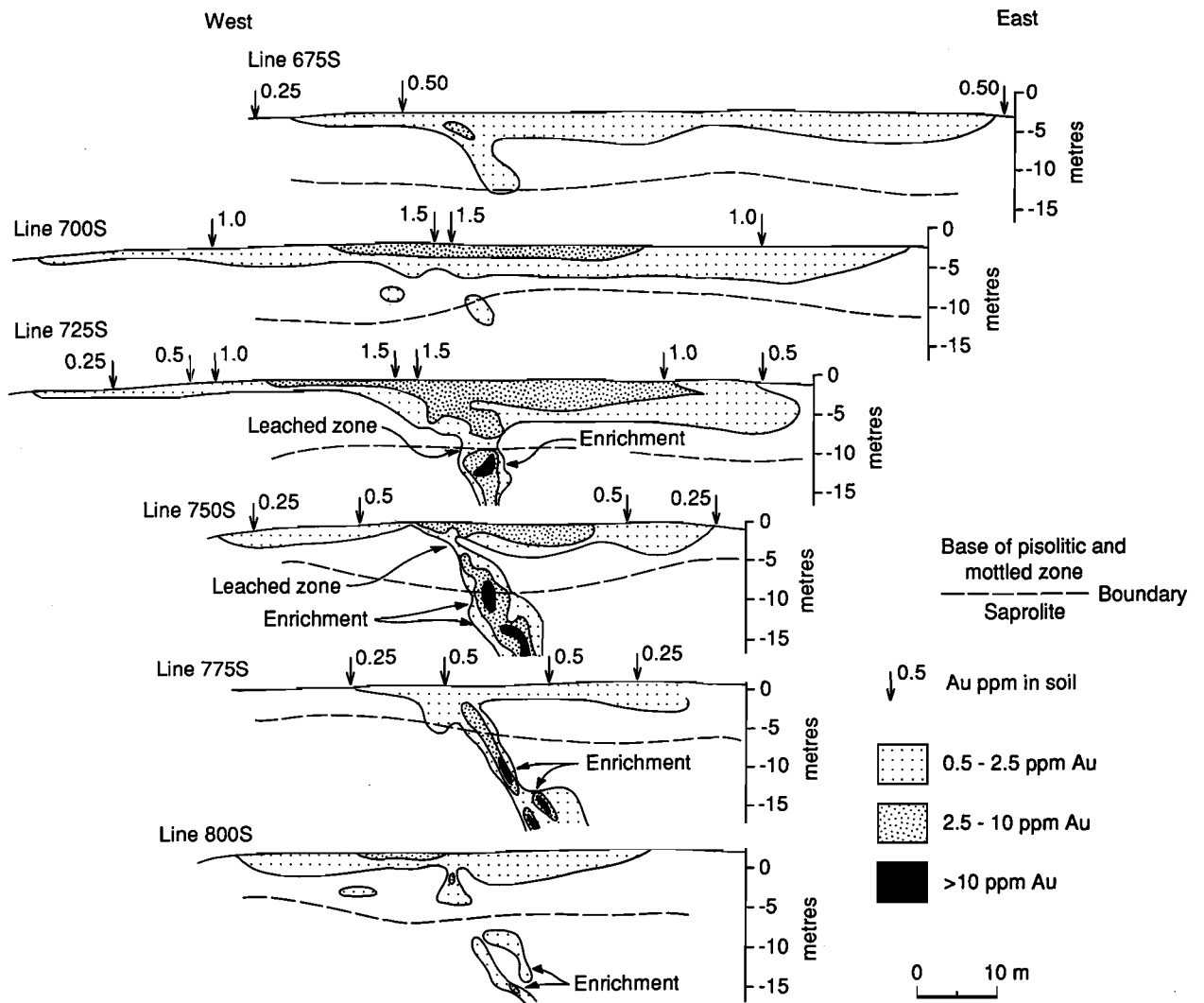


Figure 4.5 Distribution of gold in the upper regolith, Glasson deposit, Callion (after Glasson *et al.*, 1988).

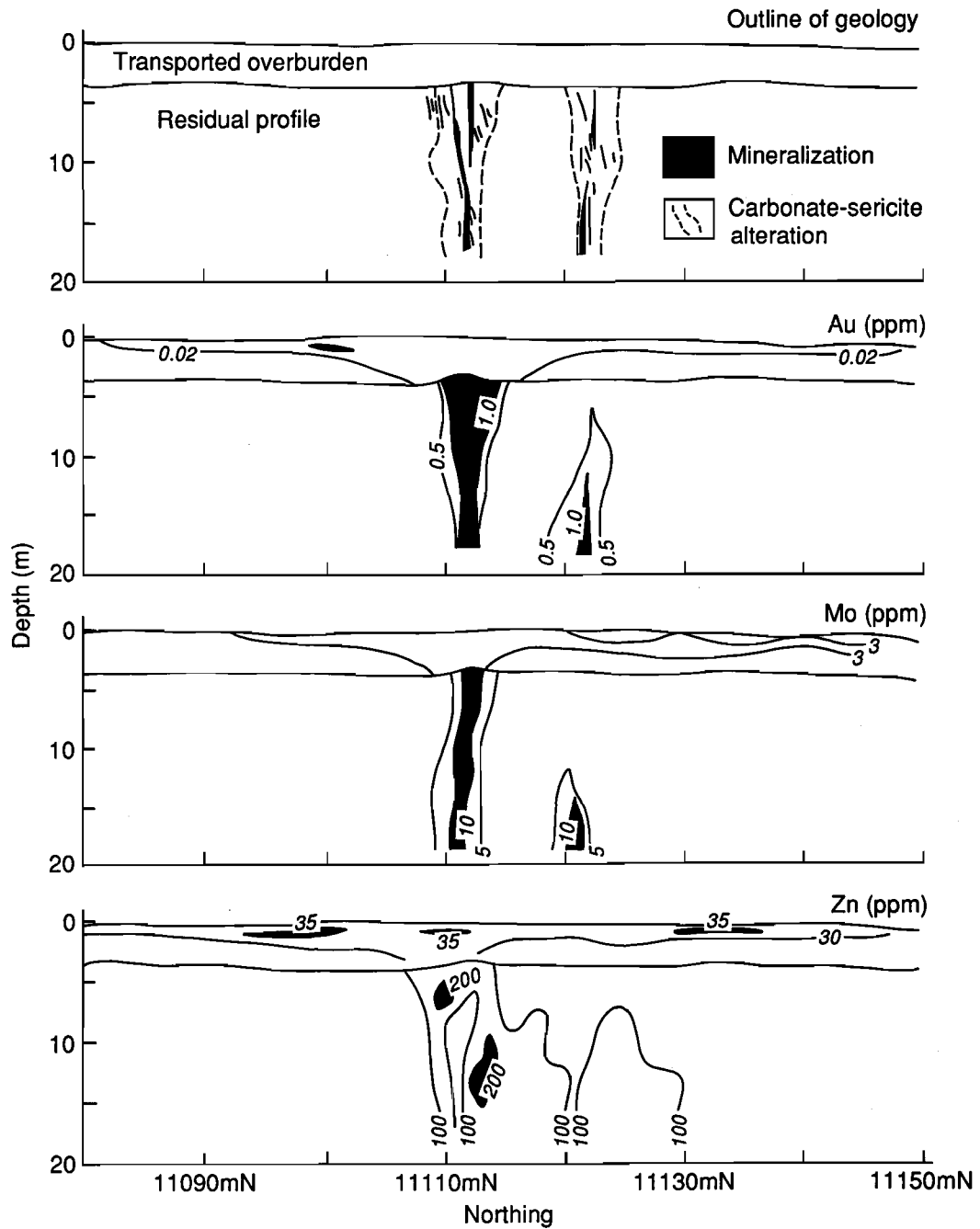


Figure 4.6

Distribution of Au, Mo and Zn around the lode system and into overlying transported overburden, Mt. Pleasant (after Lawrance, 1988).

5.0 MORPHOLOGY AND COMPOSITION OF PARTICULATE GOLD

5.1 INTRODUCTION

In lateritic regoliths, gold known or inferred to be secondary is of very high fineness (greater than 999 fine; Wilson, 1984). In comparison, free primary gold tends to be 950 fine or less, alloyed with silver and with minor amounts of a range of other metals (e.g., Cu, Hg); in the Kalgoorlie region especially, Au and Ag also occur as tellurides. It had also been established that, although much secondary gold is very fine grained ($<10\text{ }\mu\text{m}$), some is coarser and may be present as euhedral and subhedral crystals, whereas primary grains may be corroded or have Ag-poor rims of presumed secondary gold. It was therefore decided to investigate the composition and the morphology of particulate gold in order to determine whether there were any systematic variations that could be related to the evolution of the regolith or to particular environments within it. P. Freyssinet (University of Strasbourg) was conducting a similar investigation in seasonally humid tropical (savanna) environments in Mali, West Africa. He was invited to participate in the research, since the comparison between the two regions would be particularly valuable, given the assumption that the lateritic regoliths in both areas formed in similar environments, but that in Western Australia, the regolith has subsequently been modified as a result of the change to a semi-arid climate.

5.2 STUDY AREAS AND METHODS

Detailed investigations were carried out at the Zoroastrian Mine, Bardoc (Report MG58R), Beasley Creek deposit, Laverton (Report MG59R), Rand Pit, Reedy (Report MG60R) and the Mystery deposit, Mt. Percy (Report 124R). A less comprehensive study was conducted at Panglo (Report 110R) and other observations were made at Youanmi (Report 23R), Callion (Report 58R) and Telfer (Report 187R). Important comparative studies are those at Hannan South (Lawrance, 1988b), Kangaba, Mali (Freyssinet *et al.*, 1989a), Cuiaba, Mato Grosso, Brazil (Michel, 1987) and Dondo Mobi, Gabon (Colin *et al.*, 1989). The studies at Bardoc, Beasley Creek, Reedy, Mt. Percy, Kangaba and, in part, Dondo Mobi were carried out using similar procedures, namely by selecting samples from several different regolith horizons and:

1. jaw-crushing to about 5 mm and disc-grinding to 1.5 mm;
2. washing and panning to a residue of 10-20 g, by hand or using a Superpanner, and then panning the residue, again by hand or with a micropanner;
3. removing the grains and examining their sizes and morphology optically and/or by SEM. The Ag-contents of the grain surfaces were determined semi-quantitatively by energy dispersive x-ray analysis on the SEM;
4. preparing polished sections and analysing selected grains quantitatively by electron microprobe.

The results from the principal sites are summarized on Tables 5.1, 5.2 and 5.3. Examples of the grains recovered from various horizons of the profile at Bardoc are shown in Plate 5.1. It is important to note that most data refer to particles of free gold that could readily be separated by panning. A high proportion of particles smaller than $10\text{ }\mu\text{m}$ will have been lost, with moderate losses of those of $10\text{-}20\text{ }\mu\text{m}$. In some samples, recoveries were much poorer than expected from the analytical grade. This may be due to the gold being very fine grained ($<5\text{ }\mu\text{m}$) and/or enclosed within other minerals and consequently lost.

5.3 GOLD COMPOSITIONS AND MORPHOLOGY

Chemical analyses of individual grains during SEM examination or by electron microprobe demonstrated Ag to be the only element, other than gold, present as a major component. Based on the Ag content, there are two distinct groups of gold grains, one with $<1000\text{ ppm}$ Ag and one with $>4\%$ Ag. Silver-poor gold is abundant throughout the regolith in the Western Australian deposits but is only present in the upper horizon at Kangaba and Dondo Mobi. It occurs as crystals, irregular and hackly aggregates, micro-spherules, dendrites, depletion rims on Ag-rich grains and miscellaneous forms such as 'paint' and 'wire'; all such gold is considered secondary. Conversely, most Ag-bearing gold appears to be primary, an exception being some

grains from beneath the redox front at Hannan South. The Ag contents are particularly high at Mt. Percy (37% Ag), where Ag and Au tellurides are also present, and Beasley Creek (30% Ag), whereas in most other deposits, represented by Bardoc, Kangaba, Telfer (Report 187R) and Hannan South, gold tends to contain 5-12% Ag. Data from Bardoc and Kangaba suggest that the mean Ag content decreases with increased corrosion, implying progressive leaching of Ag. Alternatively, it may reflect preferential dissolution of more Ag-rich grains. Experimental data (Mann, 1989a and 1984b) indicate that Au-Ag alloys are more soluble in saline environments than pure gold, which suggests that relict primary grains will be dissolved in preference to secondary grains. The only trace element commonly detectable in the Ag-rich grains is Cu (100-3000 ppm at Bardoc, Reedy and Kangaba). Some Ag-poor grains contain trace As and Fe (<500 ppm). Unlike Ag, which is evenly distributed, these other elements occur erratically and are probably present as micro-inclusions of sulphides (primary grains) or Fe oxides (secondary).

It is difficult to establish the significance of the different morphologies and crystal habits. Crystals develop in cavities whereas irregular, xenomorphic forms develop in confined locations and bear the impressions of adjacent minerals, sometimes identifiable e.g., as quartz or striated pyrite. Freyssinet et al., (1989a) considered some smoothed, irregular masses at Kangaba to be typical of primary gold associated with sulphides; however, it is possible that some of the smoothing may be a weathering effect, perhaps due to local re-mobilization as thiosulphate complexes. In general, weathering of primary gold causes rounding of grain edges and pitting of crystal faces. Silver-poor rims may develop in some circumstances, though the mechanism is not understood (Report 4R). Some small 'secondary' grains may be the result of such rims extending and coalescing across the particle.

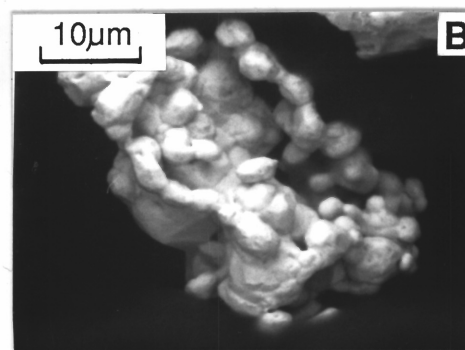
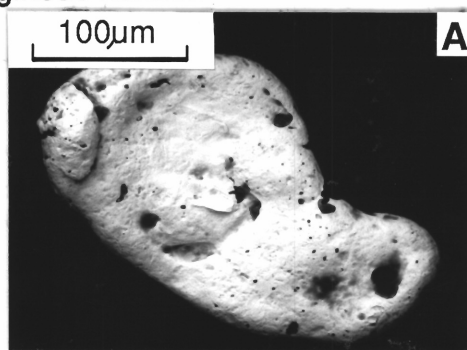
Secondary gold has many forms, as listed above. All are varieties of face-centred cubes, generally as (a) mixtures of cubes, octahedra and dodecahedra, (b) elongated on an octahedral axis, growing as parallel partial crystals, in two- and three-dimensional dendritic forms and (c) flattened pseudo-hexagonal plates. Apart from the constraints imposed by confining minerals, it is assumed that the crystal shape is a function of the environment in which precipitation takes place. For example, Gatellier and Disnar (1988) precipitated gold as pseudo-hexagonal plates and cubo-octahedral crystals by reduction from chloride solution. These forms were found together in the highly saline environment of Hannan South (Lawrance, 1988b) and crystals at Panglo, which is also very saline, are made of similar plates. The occurrence of several crystal forms together and the evidence for multi-phase gold mobilization limits further interpretation.

5.4 DISCUSSION

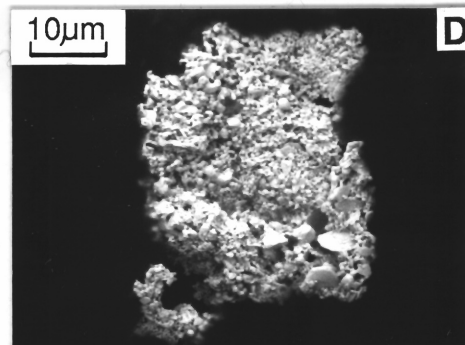
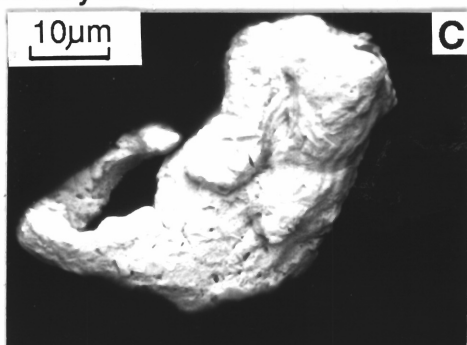
5.4.1 Savanna and rainforest environments

One of the most important features of the results is that in humid, tropical environments (Kangaba, Dondo Mobi), particulate gold is predominantly primary and remains uncorroded, or almost so, to the upper saprolite. From this level, corrosion causes pitting, rounding and a reduction in mean size; it is possible that there is also a gradual decrease in the Ag content. At Kangaba, secondary Ag-poor gold only becomes evident in the mottled and ferruginous zones, initially as rims and spherules on primary grains, and subsequently as spherules, dendrites and other forms dispersed through the ferruginous matrix. This implies that there is no mobilization of gold during the first stages of weathering and the development of much of the saprolite. There is, accordingly, no secondary concentration or dispersion halo in the saprolite. Gold mobilization is only evident in the final stages of lateritic weathering, and this results in an extensive dispersion halo (>500 m at 200 ppb Au) in the cuirasse and nodules of the ferruginous and upper mottled zones. This dispersion is attributed mainly to very fine (<1 μm) particles of secondary gold too small to be recovered by panning. Primary grains released and physically dispersed during weathering and landform reduction are found only within 10-20 m of the projected outcrop of mineralization.

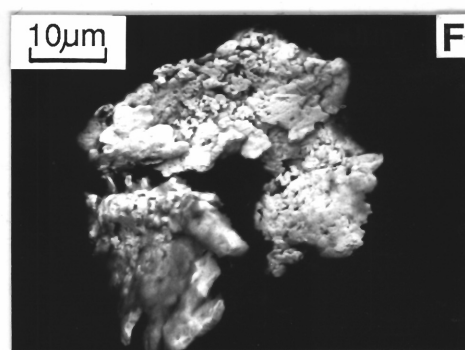
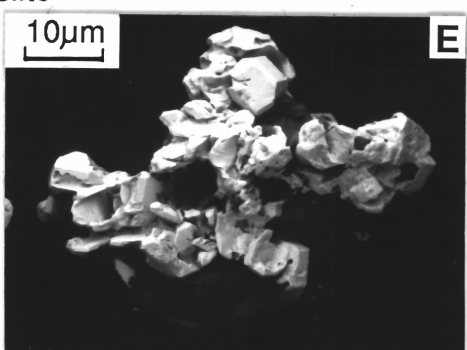
Ferruginous horizon



Mottled clay zone



Saprolite



Base of saprolite

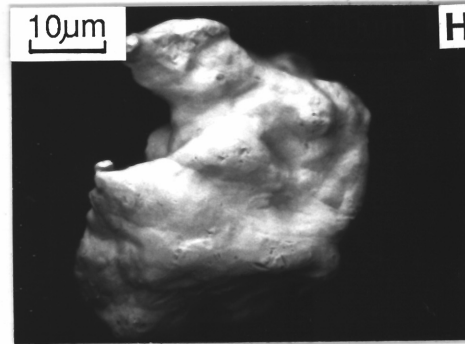
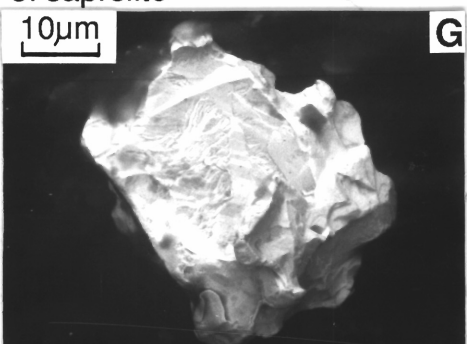


Plate 5.1 Examples of different morphologies of gold grains from the regolith at the Zoroastrian mine, Bardoc. A: etched primary grain. B: aggregate of spherules and near-octahedra of secondary gold. C: etched secondary grain. D: etched secondary particle with later spherules and pseudo-hexagonal plates adhering to it. E: aggregate of euhedral secondary crystals. F: etched secondary grain with later spherules adhering to it. G: xenomorphic primary grain. H: corroded primary grain with small secondary spherules.

Table 5.1 Comparison of gold grain morphologies

HORIZON	BARDOC	REEDY	BEASLEY CREEK
	Complete profile, 50-60 m thick. Hill crest and upper slope.	Part-truncated; 50-60 m thick; erosional plain; mid-slope.	Slightly truncated; > 200 m thick. On low rise.
Soil, calcrete	<u>Primary.</u> Coarse grains (> 150 μm), only in calcrete on laterite. <u>Secondary.</u> Coarse etched grains in calcrete on mottled clay.		<u>Primary.</u> None. <u>Secondary.</u> Two grains, 20-30 μm , one irregular, very corroded, one euhedral, pristine.
Ferruginous Zone	<u>Primary.</u> Over 40% of total. 20- > 150 μm . Most rounded, etched; rarely pristine, xenomorphic. <u>Secondary.</u> Euhedral crystal aggregates, 20-100 μm . Minor corrosion.	<u>Primary.</u> None <u>Secondary.</u> Pseudo-hexagonal crystals and aggregates, most very corroded; prismatic grains, 10-25 m, slightly etched; rounded grains, uncorroded, with adhering 1-5 μm spherules.	Derived soil. <u>Primary.</u> None <u>Secondary.</u> Two highly corroded prismatic crystals, 30-70 μm .
Mottled Zone	<u>Primary.</u> 4% of total. Strongly etched. <u>Secondary.</u> 20-125 μm . Irregular aggregates, most strongly etched, many with pristine, euhedral crystals on surfaces.		
Upper Saprolite	<u>Primary.</u> 5-10% of total. Rounded, etched, with adhering spherules of secondary gold. <u>Secondary.</u> Irregular aggregates, many with small euhedral crystals on surface. Little corrosion.	<u>Primary.</u> Present below 25 m. Rounded, etched, > 50 μm . <u>Secondary.</u> Euhedral or complex globular to hackly; etched; < 40 μm . Spherules 1-3 μm on surfaces of primary grains.	<u>Primary.</u> None. <u>Secondary.</u> Grains 50-100 μm . 10-30 m depth, highly corroded pseudo-hexagonal, prismatic and flat polygonal crystals, and pristine/weakly etched rounded and irregular grains. to polygonal, weakly etched.
Lower Saprolite	<u>Primary.</u> Over 40% of total. Rounded, etched, with Ag-depleted rims. Some xenomorphic or prismatic in wallrock, 10-20 μm . <u>Secondary.</u> Prismatic and pseudohexagonal crystals, 15-40 μm ; irregular aggregates of spherules and dendrites. Some grains corroded, others pristine.		<u>Primary.</u> 40-100 μm . Pristine or weakly etched xenomorphic grains and euhedral crystals; strongly etched, rounded grains. <u>Secondary.</u> 1 μm spherules adhering to etched primary grains; highly corroded flat, polygonal crystals, 15-30 μm .
Fresh Mineralization		Primary. 60% xenomorphic: in quartz, 20- > 50 μm , rounded, many faces; in sulphides, irregular, large flat faces; in quartz carbonate veins to 1 mm, flattened, jagged, or 10-30 μm , rounded, euhedral. 30% prismatic, 10-30 μm . Secondary. None.	

Table 5.2 Comparison of gold grain morphologies

HORIZON	MT. PERCY	HANNAN SOUTH	KANGABA, MALI
	Complete profile, 50-70 m thick. Hill crest and upper slope.	Profile 50-75 m, truncated to upper saprolite; beneath playa.	Complete profile, 50-80 m thick. Upland plateau. Savanna climate.
Ferruginous zone	<u>Primary.</u> None <u>Secondary.</u> Size 5-100 μm . 35% irregular, hackly; 35% subhedral to euhedral equant crystals; remainder anhedral or mixed type. Most strongly etched; some pristine or with some faces selectively etched.	Eroded	<u>Primary.</u> 50- > 500 μm , mean 240 μm . 90% rounded, spherical, strongly etched and pitted. <u>Secondary.</u> Spherules, 0.25-1 μm , in etch pits in primary grains and on Fe oxides. Dendrites, 10-30 μm , on Fe oxide surfaces. Ag-poor rims on primary grains. Rare spherical grains, to 200 μm
Mottled zone	<u>Primary.</u> None. <u>Secondary.</u> None.	Eroded	<u>Primary.</u> 50- > 700 μm , mean 320 μm . Polygonal, xenomorphic and hackly forms; 50% weakly etched and rounded. <u>Secondary.</u> Some spherules < 1 μm
Upper saprolite	<u>Primary.</u> Two subhedral, strongly corroded grains in mid-saprolite, 20-30% Ag. <u>Secondary.</u> Abundant, especially towards top, 15- > 100 μm ; > 50% hackly, 40% subhedral-euhedral. About one third pristine, remainder moderately to strongly etched. Corrosion increases with depth.	<u>Primary.</u> None. <u>Secondary.</u> None.	<u>Primary.</u> 100- > 1000 μm , mean 600 μm . Polygonal and xeno- morphic, with bright imprints of quartz faces. Irregular, ragged, from sulphide environ- ment. Most pristine, < 15% corroded. <u>Secondary.</u> None.
Lower saprolite	<u>Primary.</u> 50% of total. 20- > 100 μm , 20- > 90% Ag. Most strongly corroded; rarely pristine, euhedral or very irregular xenomorphic. Some Ag tellurides. <u>Secondary.</u> 20-100 μm . Mainly hackly, some euhedral-subhedral crystals. Mostly corroded. Some Ag halides, rarely with Te or coating of Au.	Above redox front. <u>Primary.</u> None. <u>Secondary.</u> Thin hexagonal and trigonal plates (15-3000 μm), octahedral crystals (5-20 μm), rare fused, part-rounded octahedra (50-100 μm) with smaller crystals and plates. Some semi-crystalline masses to 40 μm in voids; dendrites, wire, mamillary forms and coatings on fractures. Most grains part corroded, some pristine.	
Fresh mineralization	<u>Primary.</u> Subhedral to anhedral, xenomorphic; > 20% Ag. Also Ag and Ag-Au tellurides. <u>Secondary.</u> None.	Below redox front. <u>Primary.</u> Ovoid inclusions (< 1-100 μm) in outer zones of pyrite grains. <u>Secondary.</u> Smooth, rounded, Ag-bearing grains (< 20 μm) and clusters around part weathered pyrite grains. Rare grains to 100 μm in Fe oxide pseudomorphs of pyrite.	
Primary gold Ag content	Mean 37%; range 18-85%; N=21.	5-10%	Mean 4%; range 5-10%; N=235.

Table 5.3. Gold grain morphologies, Panglo and Dondo Mobi**PANGLO.**

Truncated to upper saprolite, 60-70m thick.
 Located on playa margin.

Gold panned from high grade (19-43 g/t) intersections of sub-horizontal enrichment zone in the mid to lower saprolite (37-48 m).

Grains 50-300 μm , occurring as xenomorphic forms with impressions of adjacent minerals (e.g., quartz), or of euhedral to subhedral crystals. No grains contained detectable Ag. Most grains corroded and showing etch pits. The xenomorphic grains and at least some crystals appear to be comprised of pseudo-hexagonal platelets (commonly corroded) and fine ($<5 \mu\text{m}$) spherules (commonly pristine).

DONDO MOBI, GABON.

Complete profile, $>30 \text{ m}$ thick.
 Hill crest and upper slopes; in equatorial rainforest.

<u>Soil</u>	Subhedral primary crystals, faces with pits to $10 \mu\text{m}$ and crystal edges strongly blunted. Increasingly rounded toward surface.
<u>Lateritic stone-line</u>	Subhedral primary crystals, faces with numerous pits $<2 \mu\text{m}$, crystal edges blunted.
<u>Upper saprolite</u>	Subhedral primary crystals and xenomorphic forms with sharp edges. Crystal faces unpitted, with felted, non-porous surface.

The results from Kangaba (seasonally humid savanna, annual rainfall 1300 mm) and Dondo Mobi (rainforest, annual rainfall 2000 mm) are very similar, even though in the latter area, the increased rainfall has led to the gradual destruction of the lateritic horizon to form a stone-line. The principal difference is the further dissolution of primary gold in the soil and its secondary reprecipitation to form a dispersion halo in soils and stream sediments. Only Ag-rich, presumed primary, grains were found in the very thin laterites at Cuiaba in Brazil.

5.4.2 Semi-arid environments

The principal features of the Western Australian deposits are that (a) almost all primary gold in the regolith is corroded, except that probably released from enclosing vein quartz during sample preparation, and (b) secondary gold is present in all horizons of the profile other than the near-surface leached or depleted zone, which is devoid of gold. In addition, there has commonly been considerable redistribution of gold, with leaching, reconcentration and dispersion beneath the ferruginous zone. The co-existence of both pristine and corroded grains, and the precipitation of microspherules and platelets on corroded secondary gold, indicate that there were several gold-mobilizing episodes.

5.5 CONCLUSIONS

The differences between these Australian and African deposits are due to the post-lateritic climates. Whereas in Africa, the climate has remained dominantly humid, in Australia there has been a change to semi-arid conditions, permitting gold mobilization as halide complexes in saline groundwaters. Evidence for the earlier phase is best seen at Bardoc where over 40% of gold particles in the ferruginous zone are primary. Many resemble primary grains from the equivalent horizons at Kangaba and Dondo Mobi and are interpreted as having been protected from later remobilization, e.g., within vein quartz and pisoliths. Below this level, most primary grains, which by analogy had presumably been almost unaffected by lateritic weathering, have been dissolved, only being abundant again at the base of the profile. The preservation of primary gold high in the profile was only seen at Bardoc and within quartz veins in the kaolinitic upper saprolite at Callion. Its absence at the other sites may be due to poorer protection, partial erosion (Beasley Creek, Reedy) or to greater solubility because of high Ag contents (Mt. Percy, Beasley Creek). The widespread dispersion of gold in the ferruginous zone, characteristic of lateritic deposits in Western Australia, is similar to that in humid environments and may well be inherited, at least in part. Nevertheless, it is evident that a significant proportion of this gold at Callion, Mt. Percy (Report 156R) and Mulline (Report 159R) is associated with carbonate, and hence must have been reworked under arid conditions. Other features resulting from the mobilization of gold during weathering under arid conditions are (a) depletion in the mottled and/or plasmic zones and/or the upper saprolite and (b) concentration and lateral dispersion in the saprolite. Neither feature has been reported from humid environments, although some etching and minor leaching of gold has been noted in some examples. The chemical mechanisms of gold mobilization are discussed in Sections 6 and 8.

6.0 THE CHEMISTRY OF GOLD IN THE WEATHERING ENVIRONMENT

6.1 OVERVIEW

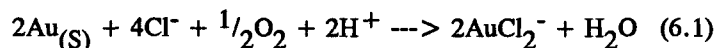
Gold is a highly inert element and is dissolved only under highly specific circumstances. Particular complexing anions and/or solution processes are required to enable groundwater mobility, as listed in Table 6.1. The various complexes become important under different chemical conditions, so that knowledge of the controls on their solubility will aid interpretation of the geochemistry of Au in various environments. These controls are discussed in detail in Report 4R, and are briefly summarized below.

Species	Possible Origin	Solubility Range
$\text{Au}(\text{OH})_2^-$	Oxidative dissolution of gold under alkaline conditions.	Oxidized; $\text{pH} > 8$
$\text{AuCl}_2^-/\text{AuCl}_4^-$	Oxidative dissolution of gold under acid/saline conditions.	Oxidized/saline/acidic
$\text{Au}(\text{HS})_2^-$	Dissolution of gold by reduced waters during early supergene alternation, or by reducing solutions generated by biological action.	Reduced/neutral $\text{Eh} < -0.1\text{V}$ $\text{pH} 6 - 9$ Total sulphur $> 0.02 \text{ M}$
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$	Weathering of gold/pyrite in neutral to alkaline solution.	Alkaline to weakly acid
$\text{Au}(\text{CN})_2^-$	Interaction of cyanide with gold.	Limited by cyanide content
Au-organic matter	Interaction of organic phases with gold.	Not certain
Colloidal gold	Formed during reduction of gold by organic matter.	Not certain

6.2 SPECIFIC COMPLEXES

6.2.1. Halide complexes

Chloride has long been suspected of being an important ligand for complexing Au (Liversidge, 1893; Krauskopf, 1951; Cloke and Kelly, 1964). Highly acid, saline and oxidizing conditions are required for dissolution of Au chloride (AuCl_2^-):



In solutions containing one mole/litre (M) chloride (35000 mg/L, i.e., about twice sea water), that are acid ($\text{pH} < 5$) and highly oxidizing ($\text{Eh} > 680 \text{ mV}$), Au concentrations of 10^{-8} M ($2 \mu\text{g/L}$) are possible (Figure 6.1). Such highly oxidizing conditions have been produced in laboratory simulations of weathering in the presence of manganese dioxide (Cloke and Kelly, 1964). In this chemical environment, the oxidation potential is controlled by the Mn^{2+}/Mn oxide redox couple, as discussed in detail in Section 7.4.

Gold chloride complexes can be precipitated by reducing conditions and, in particular, by the presence of ferrous iron, which readily reduces Au:



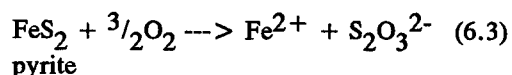
The other halides, particularly iodide, form stronger complexes with Au than chloride. Iodide generally has been considered to have a low concentration in groundwater (though hydrogeochemical investigations in the Yilgarn have suggested otherwise; Chapter 7): however enhanced levels may result from the decomposition of organic matter. Thus, iodide complexes may be important for Au mobilization in surface horizons.

6.2.2. Thio complexes

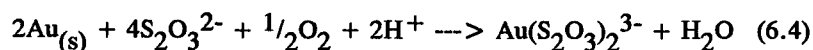
Sulphur forms a number of species with varying oxidation states from -2 to +6: among which are (from lowest to highest oxidation state) hydrogen sulphide (SH^-), solid S, thiosulphate ($\text{S}_2\text{O}_3^{2-}$), sulphite (SO_3^{2-}), and sulphate (SO_4^{2-}). Solid S obviously will not mobilize gold, and sulphate, the most stable form of oxidized sulphur, does not complex Au. The important species for Au mobilization are considered to be hydrogen sulphide (as bisulphide) and thiosulphate, as described below.

Gold bisulphide complex $[\text{Au}(\text{SH})_2^-]$ is mobile only under highly reducing conditions, because of the tendency of the sulphide ion to oxidize. This complex is of importance for the hydrothermal transport of Au (Seward, 1973, 1982), but has only a restricted occurrence in the supergene zone. Sulphide may exist in solution at 10-1000 mg/L in the vicinity of pyrite deposits (Subzhiyeva and Volkov, 1982): assuming a total dissolved S content of 700 mg/L, under optimum conditions, total dissolved Au could equal 1200 $\mu\text{g/L}$.

In the presence of oxygen, sulphide will be oxidized to sulphate, with acid production (Equation. 7.1). However, under neutral to alkaline weathering conditions, appreciable amounts of the intermediate product, thiosulphate, may be formed (Granger and Warren, 1969; Goldhaber, 1983), e.g., during pyrite oxidation:



The thiosulphate ion is meta-stable (i.e., it is thermodynamically unstable but may exist in solution for long periods due to its kinetic inertness; Rolla and Chakrabarti, 1982). It can dissolve Au even under weakly oxidizing conditions (Lakin et al., 1974; Webster, 1986; Webster and Mann, 1984):



Appreciable thiosulphate production will only occur if the pyrite is buffered by alkaline species. Mann (1984b) calculated that 400-800 g of CaCO_3 are required for every 240 g of FeS_2 to maintain alkaline conditions for thiosulphate production, and therefore significant Au thiosulphate mobilization. The Au-thiosulphate complex is soluble under alkaline, neutral and slightly acid conditions. Other factors that could influence the stability of the Au-thiosulphate complex include organisms or elements with variable oxidation states, e.g., Fe or Mn. The solubility behaviour of Au in S-rich solutions is summarized in Figure 6.2.

6.2.3. Cyanide complexes

Gold forms the very strong $\text{Au}(\text{CN})_2^-$ complex, which is stable over a wide range of conditions (Boyle, 1979), with the limiting factor to solubility being the concentration of available cyanide. Certain plants and micro-organisms are known to release cyanide (Lakin et al., 1974; Sneath, 1972) and can accumulate appreciable Au (Warren, 1982). Cyanogenic bacteria can produce up to 200 mg/L cyanide *in vivo* (Rodgers and Knowles, 1978), and can solubilize up to 215 mg/L Au from the pure metal (Smith and Hunt, 1985). Such bacteria are frequently associated with plants, soil and organic matter (Corpe, 1951; Saupe et al., 1982), and zones such as a highly organic horizon or the immediate surroundings of an active root of a cyanogenic plant could contain elevated levels of cyanide and cause Au mobility. As with the Au thiosulphate complex, decomposition of the cyanide and precipitation of the Au may occur as the result of specific chemical or biological factors.

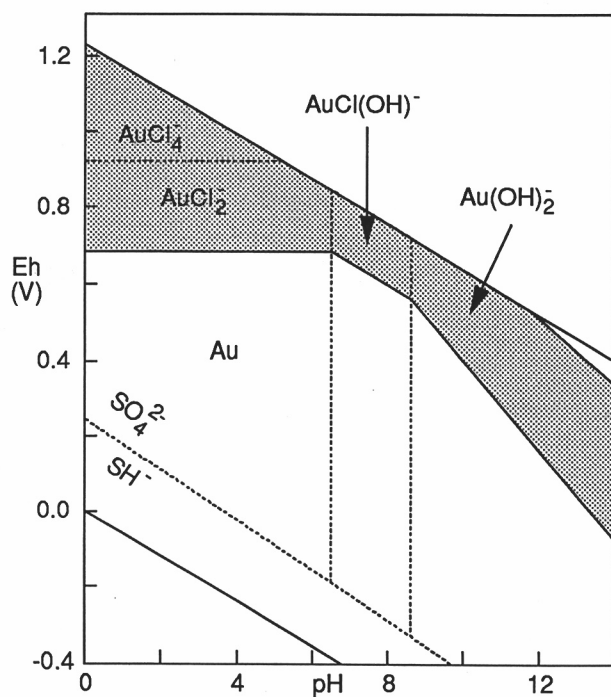


Figure 6.1: Gold speciation in 1 M NaCl. The shaded area indicates where Au solubility is greater than 2 $\mu\text{g/L}$ (10^{-8} M).

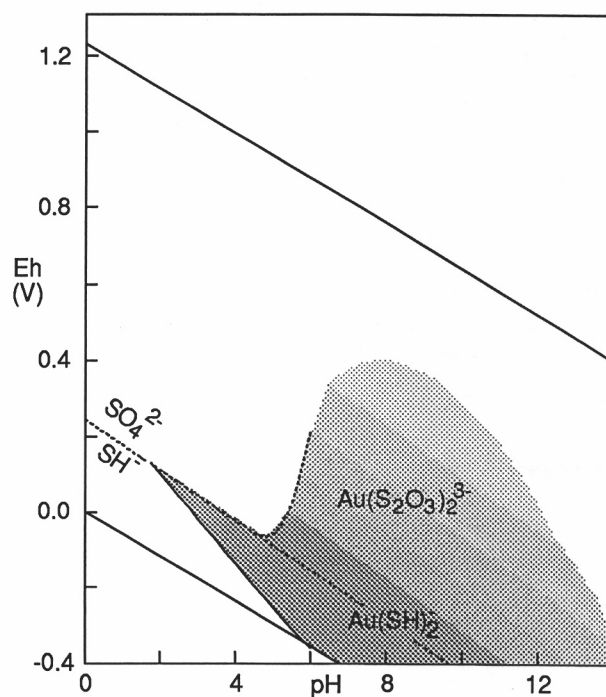


Figure 6.2: Gold speciation in 0.01 M S. The shaded area indicates where Au solubility is greater than 2 $\mu\text{g/L}$ (10^{-8} M).

6.2.4. Organic complexes

Numerous studies (e.g., Freise, 1931; Fetzner, 1934, 1946; Ong and Swanson, 1969; Baker, 1973, 1978; Boyle et al., 1975; Roslyakov, 1984; Grégoire, 1985; Fedoseyeva et al., 1986; Gatellier and Disnar, 1988) have indicated highly varying interactions between Au and organic matter. Whereas solid organic matter and some soluble organic phases have been shown to remove Au from solution, other soluble organic phases have been found to dissolve Au. In general, Au-organic interactions are highly dependent on the chemistry of the organic material, the concentrations of the phases, and the chemistry of the groundwater.

Gold readily forms colloids or sols (i.e., molecular aggregations up to 5 μm in size) and such chemical species have been known for centuries (Boyle, 1979). Colloidal Au stabilized by organic matter has been observed in the laboratory (Goni *et al.*, 1967; Ong and Swanson, 1969; Ong et al., 1969; Fedoseyeva et al., 1986), and has been postulated as an important mechanism for the mobilization of Au. These sols are negatively charged and therefore could be mobile in negatively charged soils, precipitating where they contact a soil horizon containing positively charged minerals such as Fe oxides. However, attempts to demonstrate the natural occurrence of colloidal Au have been unsuccessful (Boyle, 1979; Kolotov et al., 1980), possibly due to experimental difficulties at low concentrations of dissolved Au. Thus, on the basis of the above work, it seems that colloidal Au will only be important for Au mobility, if at all, in the presence of dissolved organic matter. Further work on Au sols was done as part of this project (Report 128R). In general, (as described in Section 9.4) Au was found to readily form a stabilized sol in the presence of soluble matter, though in a manner that was dependant on a number of factors, including concentrations of Au and organic matter, the source of the organic matter and the presence or absence of light. This complexity of factors can readily explain the variety of results from previous work.

6.2.5. Biological effects

Many of the chemical species that may cause Au mobility (iodide, sulphide, thiosulphate, cyanide, organic matter) are partly or extensively influenced by biological factors. Thus, soil organisms such as bacteria, fungi or plants may have major effects on Au mobility. Many plants can accumulate or adsorb Au (Shacklette et al., 1970; Kaspar et al., 1972; Girling et al., 1979; Warren, 1982; Smith and Keele, 1984), and represent a useful exploration sample medium. Some plants not only accumulate Au but may be important in its redistribution, taking up Au at depth and releasing it at the surface as litter (Erdman and Olson, 1985). This hypothesis may explain zones of depletion and concentration in surficial soil horizons. Work done as part of this project on the use of plants in exploration is described in Section 11.

In addition to plants and plant products, bacteria and other micro-organisms may have a significant influence on Au solubility and even have value in Au exploration (Watterson, 1985). Bacteria commonly alter the surrounding chemistry by catalyzing reactions; for example, sulphur bacteria may cause Au to dissolve by initiating pyrite oxidation or to precipitate by initiating the oxidation of thiosulphate ligands (Postgate, 1951). Certain species of bacteria may release cyanide (Section 6.2.3), affecting Au solubility, whereas other bacteria could cause significant Au solubility by releasing amino acid ligands (Korobushkina et al., 1974; 1983).

7.0 HYDROGEOCHEMISTRY OF GOLD

7.1 INTRODUCTION

Investigations of the hydrogeochemistry of mineralized areas have the objective of advancing knowledge of groundwater characteristics, particularly in reference to the formation of geochemical haloes in the regolith and the exploration potential of groundwater sampling in exploration. Specific fields of interest are:

- (i) what ions cause mobility of gold, and how these ions are influenced by groundwater chemistry and water-rock interactions;
- (ii) the chemical and geological factors influencing the chemistry of waters in the Yilgarn Block;
- (iii) use of gold and other pathfinder elements in water as an exploration tool;
- (iv) development of techniques for analysis of groundwater data from mineralized areas;

Hydrogeochemical investigations for this Project have been concentrated on the Panglo gold deposit (Report 125R), in conjunction with other investigations into the geochemistry and mineralogy of the regolith (Reports 32R, 42R and 143R), and on the exploration potential of soils and plants at this site (Report 129R). The observed controls on the groundwater chemistry from the underlying geology, weathering processes and hydrology are summarized below.

7.2 SITE CHARACTERISTICS

The Panglo gold deposit is located some 30 km north of Kalgoorlie. The area has an arid climate with an average annual rainfall of about 250 mm, most of which falls during the cooler months of May to August. The geology of the area and the location of the supergene Au expression are shown in Figure 7.1. Fifty water samples were taken, both from depth (down to 50 m below surface) and close to the surface, and were initially classified in terms of their geological environment:

- Sf: the shale/siltstone system in the south-east.
- M-Sf: the interface of the mafic/sediment and shale/siltstone systems.
- M-S: the mafic/sediment system hosting the gold mineralization.
- M-U: the interface of mafic and ultramafic rocks (2500E / 4600-4800N).
- U: a major ultramafic rock unit (at about 2400E / 4050-4300N).

7.3 MAJOR ELEMENT HYDROGEOCHEMISTRY

There is an increase in groundwater salinity with depth. All deep waters are highly saline [total dissolved solids (TDS) > 100,000 mg/L], are less acid (pH > 5.5) than the shallow waters and have similar relative compositions, suggesting only minor groundwater/rock interactions at depth. In comparison, the shallow waters in contact with the oxidized, weathered rocks have compositions highly dependent on the lithology, implying major interactions between the water and the regolith.

The waters are dominated by Na¹ and Cl, and most of the major ions show a very strong correlation with TDS, with the principal exceptions of Ca and HCO₃, due to precipitation of Ca as gypsum and loss of HCO₃ with acidification. The Panglo waters have higher proportions of Na and Cl and lower proportions of Mg, Ca, Sr and SO₄, with Br and K being dramatically lowered (by about 80% and 90%, respectively), relative to sea water. The reduced K concentration could conceivably be due to a number of factors, such as incorporation into alunite or adsorption by vermiculite or smectite (Report 125R; Section 3.4.4). However, Br is highly soluble, even in hypersaline brines, and therefore the Br depletion strongly suggests that most of the present salinity has been caused by dissolution of halite (observed in the profile; Reports 32R and 42R).

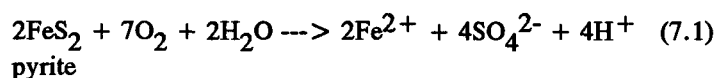
¹Note that in general ions will be denoted purely by symbol, without valence information: *i.e.*, Cl rather than Cl⁻

rather than by evaporation. Presumably, halite was deposited during a previous period when the groundwaters were more saline than present.

7.4 pH/Eh DATA

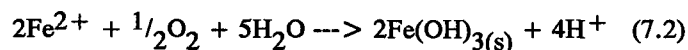
The pH and Eh of groundwaters describe important chemical attributes. The pH is the measure of proton (H^+) activity and the Eh is an analogous measure of the electron activity. Low Eh values (say, less than 200 mV) indicate reducing solutions, which will tend to be rich in reduced species (e.g., Fe^{2+} or SH^-), and high Eh values (greater than 500 mV) indicate oxidizing solutions, which will tend to contain high concentrations of oxidized species (e.g., $AuCl_4^-$). Eh is controlled by reduction-oxidation couples such as Fe^{2+}/Fe^{3+} or O_2/H_2O_2 , depending on the chemical environment.

There is an inverse relationship between soluble Fe (present as Fe^{2+}) and Eh for the Panglo water samples. The soluble Fe is probably derived from the oxidation of pyrite and other sulphide minerals. Pyrite oxidation occurs in two stages, both of which may generate acidity. The first reaction is the generation of sulphate:



This reaction generally occurs at depth. A number of the more Fe-rich (> 0.5 mg/L Fe) waters are near neutrality, particularly those sampled from depth. The sulphide oxidation step (Equation 7.1) is limited by diffusion of oxidizing species such as O_2 , and therefore acid production may be neutralized by other reactions such as carbonate or feldspar weathering.

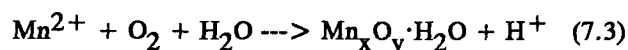
The second process, which occurs closer to the surface, is the oxidation and hydrolysis of Fe ('ferrolysis'; Brinkman, 1977), which also generates acidity:



Decoupling of the two components of pyrite oxidation (Equations 7.1 and 7.2) is commonly observed (Blowes and Jambor, 1990). As the upper weathered profile in which ferrolysis occurs probably does not contain alkaline minerals such as carbonates, shallow groundwaters may become highly acidic. The waters will then be buffered by the dissolution of clay minerals such as kaolinite, which reprecipitate as acid sulphate minerals, e.g., alunite [$KAl_3(SO_4)_2(OH)_6$], giving an acidity limit of about pH 3.

Ferrolysis (Equation 7.2) is also important in that it provides one of the major pH/Eh controls on groundwaters, and sets the lower limit on Eh for these waters. It also precipitates Fe, giving groundwaters whose Eh values are no longer controlled by Fe. Under these conditions, Eh may be controlled by the O_2/H_2O_2 couple (Sato, 1960). This couple has slow kinetics (i.e., the redox reaction is slow) and the solution will have poor redox stability. According to Sato (1960), such waters are commonly found in well oxidized systems. Such waters are not redox active, being neither strongly reducing nor strongly oxidizing.

As the groundwater becomes further oxidized, Mn^{2+} may also oxidize and hydrolyse:



This reaction is the Mn equivalent of ferrolysis and may control the Eh and pH of a solution in an analogous manner. The zone of Mn oxidation appears to be the upper limit for the Eh of groundwater at Panglo (Figure 7.3). The oxidized acidic solutions, in particular, closely follow the line of Mn oxidation. As will be discussed further in Section 7.6, this reaction is critical to Au mobility, as it enables solutions to reach sufficiently high oxidation potentials for the oxidation of native Au.

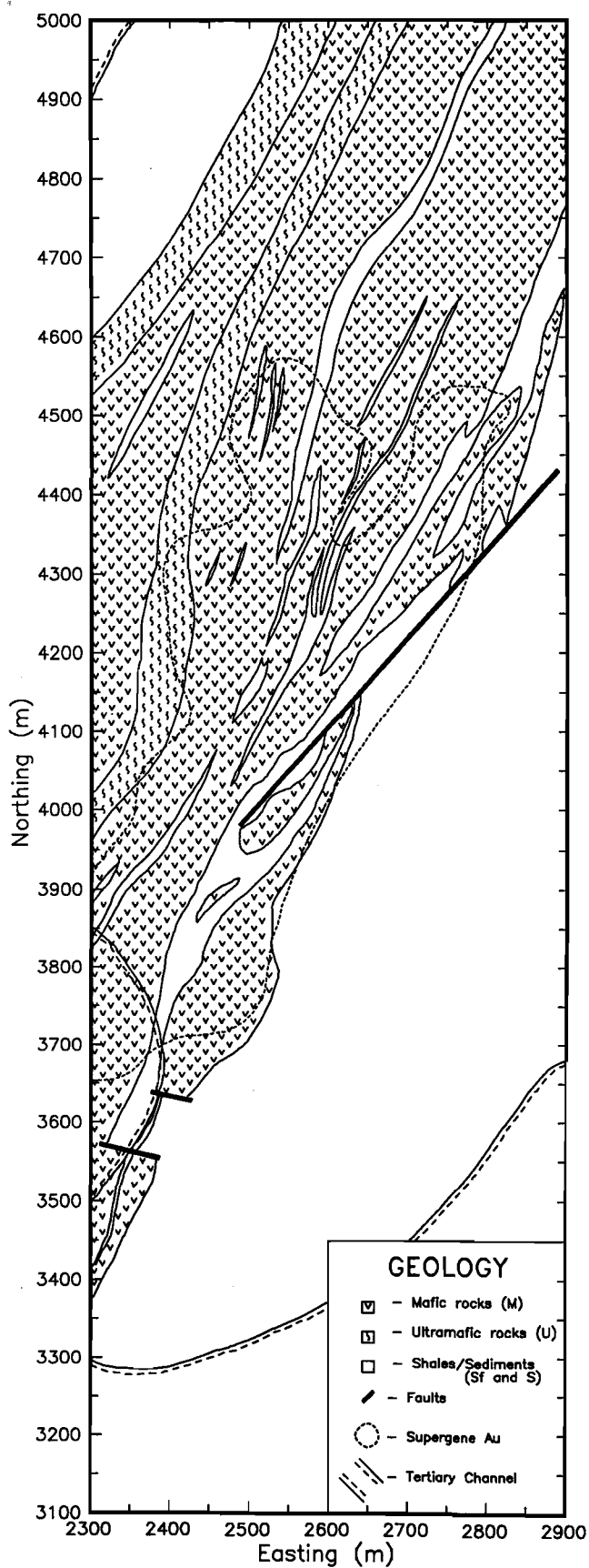


Figure 7.1: Geology and supergene expression of Au, Panglo

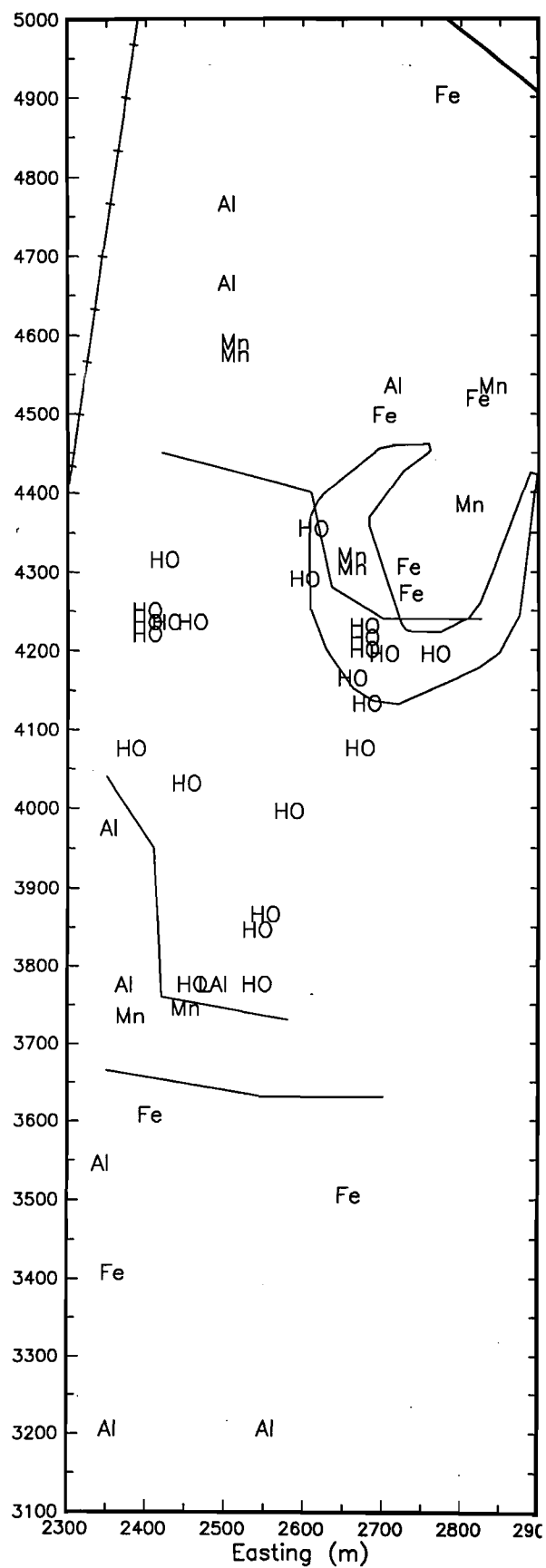


Figure 7.2: Sample pH/Eh group (Section 7.4), with the Trial Pit shown in outline.

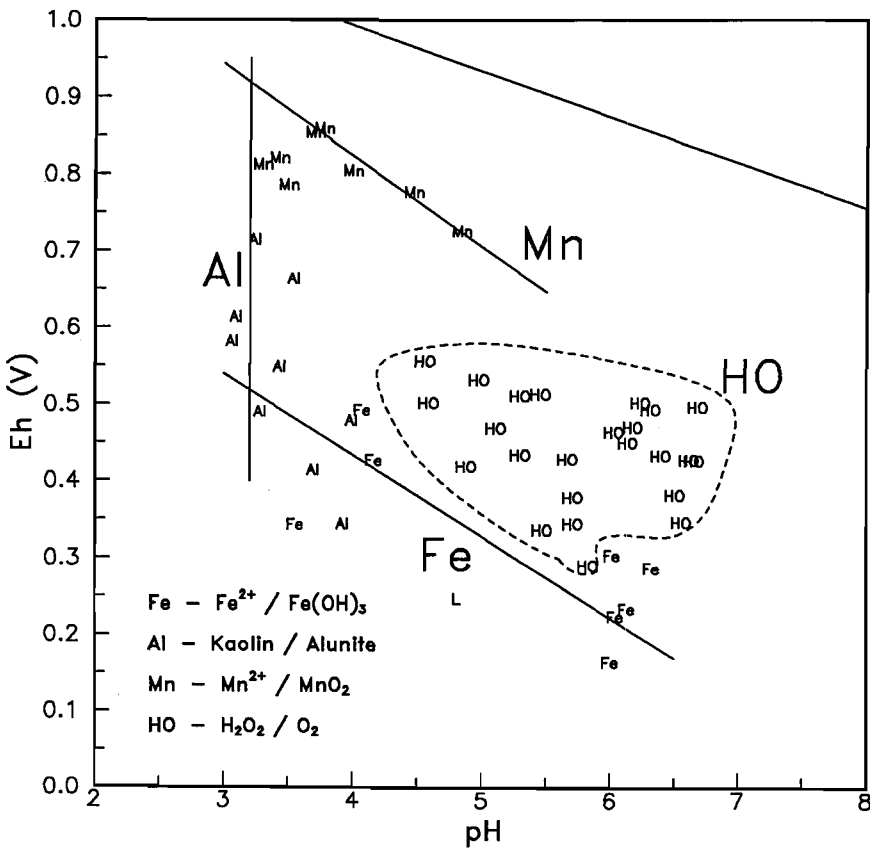


Figure 7.3: Hypothesized pH/Eh control on groundwaters at Panglo. See Section 7.4.

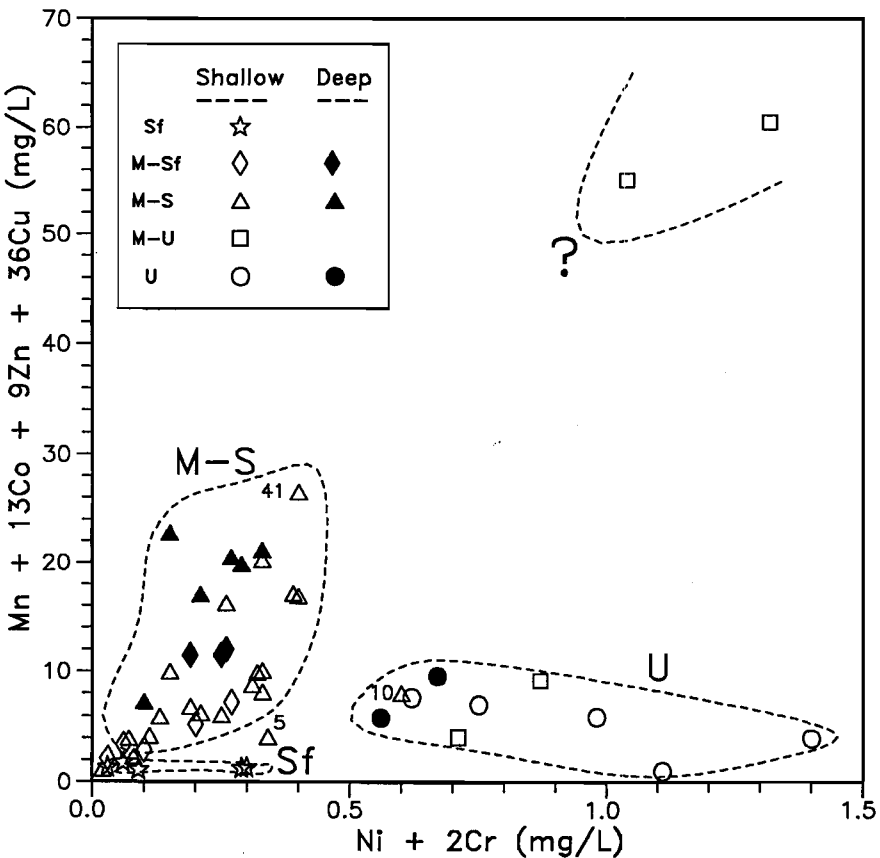


Figure 7.4: Mafic vs. ultramafic indices for groundwaters at Panglo. See Section 7.5.

Table 7.1: Chemical characteristics of the pH/Eh classes.

Group	Description	Characteristics
Fe	"Fe rich"	Fe > 0.5 mg/L
HO	"Moderately oxidized"	$4.5 \leq \text{pH} / \text{Fe} < 0.5 \text{ mg/L}$
Al	"Acid / Al-rich"	$\text{pH} < 4 / \text{Eh} < 0.72 \text{ V} / \text{Fe} < 0.5 \text{ mg/L}$
Mn	"Oxidized / Mn rich"	$\text{Eh} > 0.72 \text{ V} / \text{Mn} \geq 0.5 \text{ mg/L}$

Based on these observations, the Panglo groundwaters were divided into four major categories, as summarized in Table 7.1, with pH/Eh characteristics as shown in Figure 7.3. The major distinction between the OH and the Al Groups is the higher acidity of the Al waters. The OH waters ($\text{pH} \geq 4.5$) include the waters contacting ultramafic lithologies, and some of the deeper water samples (which are either OH or Fe waters), whereas the Al waters occur within the shale and mafic lithologies. The distributions of the various postulated pH/Eh water groups in the mine area are shown in Figure 7.2, which also shows the position of the Trial Pit excavated in 1989. A number of zones are suggested:

- (i) a northern zone, also encompassing about half of the Trial Pit area, which has group Fe waters at depth, and group Mn and Al waters closer to the surface. The high Fe contents of the deeper waters indicate significant pyrite weathering (Equation 7.1). Further oxidation of the Fe^{2+} closer to the surface has produced highly acid conditions (Equation 7.2). As these acid groundwaters oxidize further, Mn^{2+} oxidizes and surface solution Eh levels are controlled by the Mn couple (Equation 7.3). These waters are also highly enriched in Mn (partially explaining the high Eh conditions) and a number of other metals (Co, Zn, Cu, Ni, Au) and halides (Br and I). This northern area of Panglo may be actively weathering, possibly due to enhanced groundwater flow, for example, along shear zones.
- (ii) a zone comprising the southern part of the Trial Pit area (about 4300N), south to about 3750N. This has *all* of the group OH waters, both at depth and at the surface. This zone may represent an area poor in sulphide mineralization (or where there is little active sulphide weathering), resulting in little Fe release, and more neutral groundwater conditions. Note that there is no gross difference in the geology of regions (i) and (ii), and the pH/Eh differences seem to be due primarily to the degree of weathering.
- (iii) a complex zone at about 3750N, with waters of various pH/Eh groups. The presence of Fe in some samples and acid conditions in others may represent an area with minor sulphide weathering.
- (iv) a clay pan zone south of 3750N with characteristics suggesting more stagnant conditions - high Fe in the surface waters, low dissolved oxygen and commonly malodorous.

These pH/Eh zones occur as a result of variations in the bedrock geology, weathering reactions and the flow characteristics of the groundwater drainage system. Their spatial distribution is different from the strike of the geology, and so they represent an additional controlling factor on the hydrogeochemistry of the site. In particular, the distributions of various elements which are strongly controlled by pH (e.g., As) or Eh (e.g., Au) will reflect the distribution of the various pH/Eh environments.

7.5 GEOLOGICAL PATTERNS IN GROUNDWATER

The concentrations of several elements in groundwaters may be dependent on the lithology from which the water sample was taken. Thus the elemental compositions of waters from the shale unit in the south-west region of the study area (Figure 7.1) differ markedly from waters contacting the mafic or ultramafic lithologies with:

- (i) proportionally lowered Br and Sr;
- (ii) very low concentrations of Mn, Co, Zn, Cu, Ni, Cr, Sc and Au;
- (iii) possible low concentrations of I, Ag, and Bi.

The lower concentrations of base metals, despite most of the shale waters being acid, suggest that the shale system is strongly depleted in "available metals". Analyses of weathered and unweathered shale, mafic and ultramafic samples (Reports 32R, 42R and 143R) indicate that the shales have lower Mn, Ni, Zn, Co, Sc, Cu and Cr contents than the mafic and ultramafic materials. Comparison of the mafic and ultramafic waters indicates that each group has a particular 'signature'. The mafic waters are enriched in Mn, Co and Zn, and depleted in Ni, Cr, Sc, Ag and Bi, relative to the ultramafic waters. These characteristics are generally in accordance with the composition of mafic and ultramafic rocks.

These observations were also supported by statistical analysis (Report 125R; Section 3.9), showing specific correlations between elements enriched in 'mafic' waters, and between elements enriched in 'ultramafic' waters. Additional observations of ultramafic correlations in the 'mafic' waters and in the deep waters suggest a minor 'ultramafic influence' in other waters, possibly due to these waters having previously passed through ultramafic lithologies. Thus, though they have now equilibrated with mafic lithologies and become enriched in the 'mafic' elements, they still carry a 'relict' signature of elements (e.g., Cr, Sc, Bi, Ag) dissolved during contact with ultramafic material.

There are two groups of waters associated with ultramafic lithologies (Section 7.2), namely the U waters, which represent the principal ultramafic unit (Figure 7.1), and the M-U waters, which appear to be located close to the interface between mafic and ultramafic rocks. These waters differ markedly in pH. The M-U waters have a pH of 3.3 - 4.8, whereas the U waters are less acidic than any other surface water groups (pH 5.7 - 6.3), presumably as a result of the more basic nature of the ultramafic rocks. The pH differences may also be related to differing degrees of weathering. The M-U waters occur in the northern section of the study area, which has (as described above) pH, Eh and elemental abundances suggesting more intensive weathering.

The U and M-U waters also differ in composition. The U waters are strongly enriched in Si, Cr and Ni. The M-U waters have higher Ni concentrations than the U waters, but have relatively low Cr concentrations. One explanation is that some Cr in ultramafic rocks occurs in a readily dissolved form, whereas the Ni does not. For example, both Cr and Ni occur in chlorite, which is readily weathered, whereas Ni (but not Cr) is found in talc, which is resistant to weathering (Report 143R). Thus, it is conceivable that the high Cr and Si in the U waters results from weathering of chlorite. The acidic M-U waters are contacting more intensely weathered materials, from which all of the chlorite and contained Cr and Ni has been removed, so that Cr is no longer dissolving. However, appreciable Ni may still be dissolving, due to the weathering of talc.

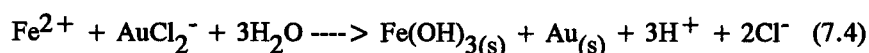
The clear chemical differences between waters contacting various lithologies can be used for classification. Although reasonable distinctions were achieved with very simple bi-variate plots (such as Co vs. Ni), the best classification was obtained by using multi-variate plots, as illustrated in Figure 7.4. In this plot, the X-axis ($\text{Ni} + 2\text{Cr}$) represents an 'ultramafic index' that efficiently separates the ultramafic rocks from the other rock types. The Y-axis ($\text{Mn} + 13\text{Co} + 9\text{Zn} + 36\text{Cu}$) represents a 'mafic index', which was calculated in such a way that each element makes a similar contribution to the index. Waters contacting the three different lithologies are clearly resolved using this plot, and the few outliers appear to be misclassifications, rather than exceptions to the scheme.

The spatial distributions of the mafic and ultramafic indices are shown in Figures 7.5 and 7.6. The high values for the ultramafic index delineate the position of the ultramafic rocks, whereas high values for the mafic index occur across the northern part of the study area, indicating that the northern region of the study area is the zone of the most pronounced acid weathering, as suggested by the pH/Eh data (Section 7.4).

It should not be assumed that waters from another site will plot in the domains given in Figure 7.4. Groundwater metal concentrations are functions of a number of site-dependent factors such as pH, salinity and Eh, in addition to the metal concentrations in the rocks or weathering minerals. However, this methodology could yield a comparable multi-element plot that would enable a site-specific classification.

7.6 GOLD HYDROGEOCHEMISTRY

In comparison with other elements (Section 7.5), the distribution pattern of dissolved Au at Panglo does not show any clear correlation with geology or pH. Gold would be expected to be mobilized as the AuCl_2^- or AuI_2^- complexes in these waters, due to the acid and saline nature of the groundwaters (Report 4R; Section 4.3). The control of Au solubility via redox reactions is demonstrated in the plot of Au vs. Fe (Figure 7.7). The relationship between the aqueous concentration of these two ions is totally antipathetic *i.e.* Au is only observed above the detection limit where Fe is less than 0.1 mg/L. This is due to the strong reducing capacity of the ferrous ion:



A similar, but less marked relationship is observed for Au vs. Eh (Figure 7.8). Samples plotting to the right of the 2 $\mu\text{g/L}$ line in Figure 7.8 should (theoretically) contain greater than 2 $\mu\text{g/L}$ Au, whereas samples plotting left of the 0.02 $\mu\text{g/L}$ line should contain less than 0.02 $\mu\text{g/L}$ Au. Actual values more or less follow this trend. The most oxidized waters ($\text{Eh} > 0.7 \text{ V}$) have Au concentrations that, though very high (up to 4 $\mu\text{g/L}$), were well below the theoretical concentration for equilibration with Au metal at the Eh values recorded for those waters. However, other factors, such as sorption of Au onto Fe or Mn oxides, may reduce concentrations of soluble Au, even in highly oxidizing waters.

The highly oxidizing conditions appear to have been generated by the Mn redox couple (Section 7.4). This is demonstrated in Figure 7.9, which shows the pH/Eh characteristics of the waters, and the postulated redox controls (compare with Figure 7.3), with conditions that are sufficiently oxidizing for 0.2 $\mu\text{g/L}$ Au to dissolve (Figure 6.1) represented by the shaded area. This area only includes those waters hypothesized to be controlled by the Mn couple (Equation 7.3). These results support other studies that indicate the importance of the Mn couple for oxidative AuCl_2^- dissolution (Miller and Fisher, 1973). The hypothesized dissolution of Au at Panglo is directly analogous to laboratory experiments in which Au was readily dissolved by a mix of Au metal, MnO_2 , H_2SO_4 and NaCl (Cloke and Kelly, 1964).

The dissolved Au distribution would be expected to be strongly spatially controlled by the different pH/Eh zones (Figure 7.2). Indeed the highest Au concentrations are found in the northern part of the study area (Figure 7.10), which is the zone of enhanced pH and Eh (Sections 7.4 and 7.5). Thus, Au concentration in water is dependent not only on the distribution of solid Au, but also on the general hydrogeochemistry of the groundwaters.

Speciation analyses for Au indicated that it will occur in most of the waters as AuI_2^- , rather than AuCl_2^- , as a consequence of the high abundance of I in the Panglo groundwaters (up to 2 mg/L; average 0.5 mg/L), in comparison with seawater (0.06 mg/L). This high I concentration is observed even under highly oxidizing conditions, despite the theoretical high volatility of I as I_2 gas under these conditions (Fuge, 1990), and is consistent with suggestions that I behaves as a chalcophile element, with potential as an indicator of mineralization (Fuge et al., 1986). This effect may indicate enrichment of I within the mineralized area (125R). Although the possibility of Au mobilization as the iodide complex has been suggested by previous

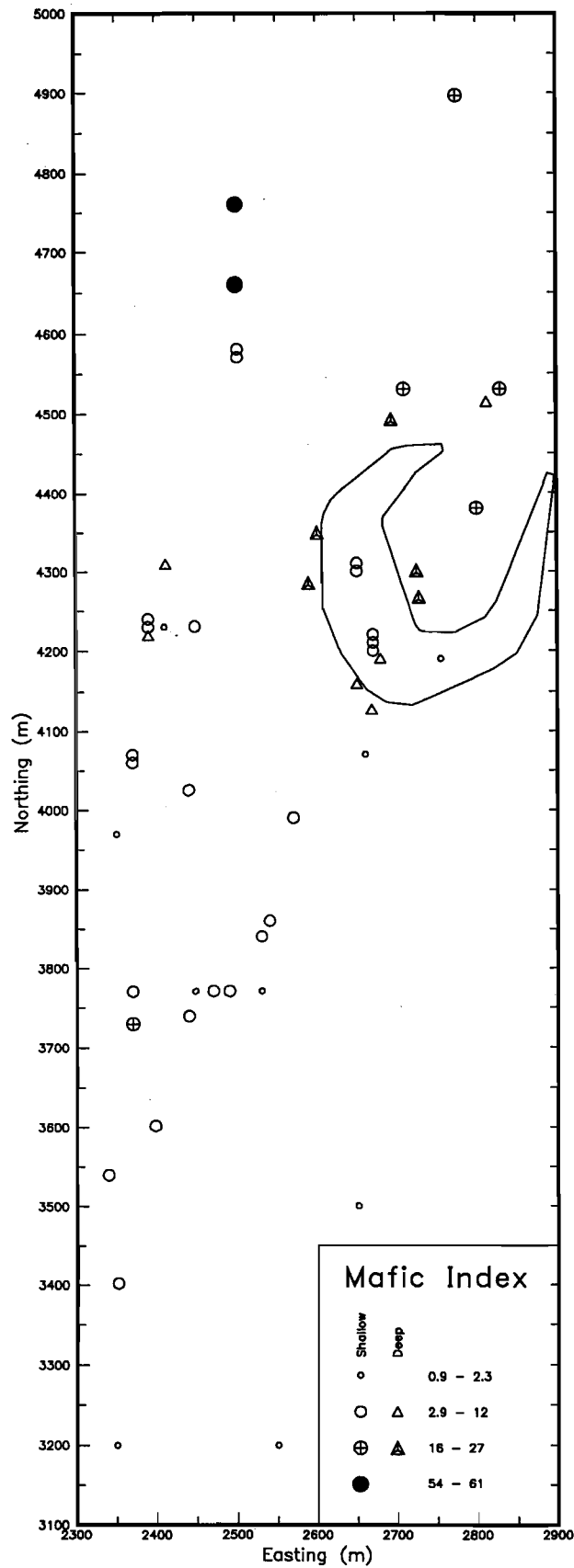


Figure 7.5: Spatial distribution of the mafic index ($Mn + 13Co + 9Zn + 36Cu$) at Panglo.

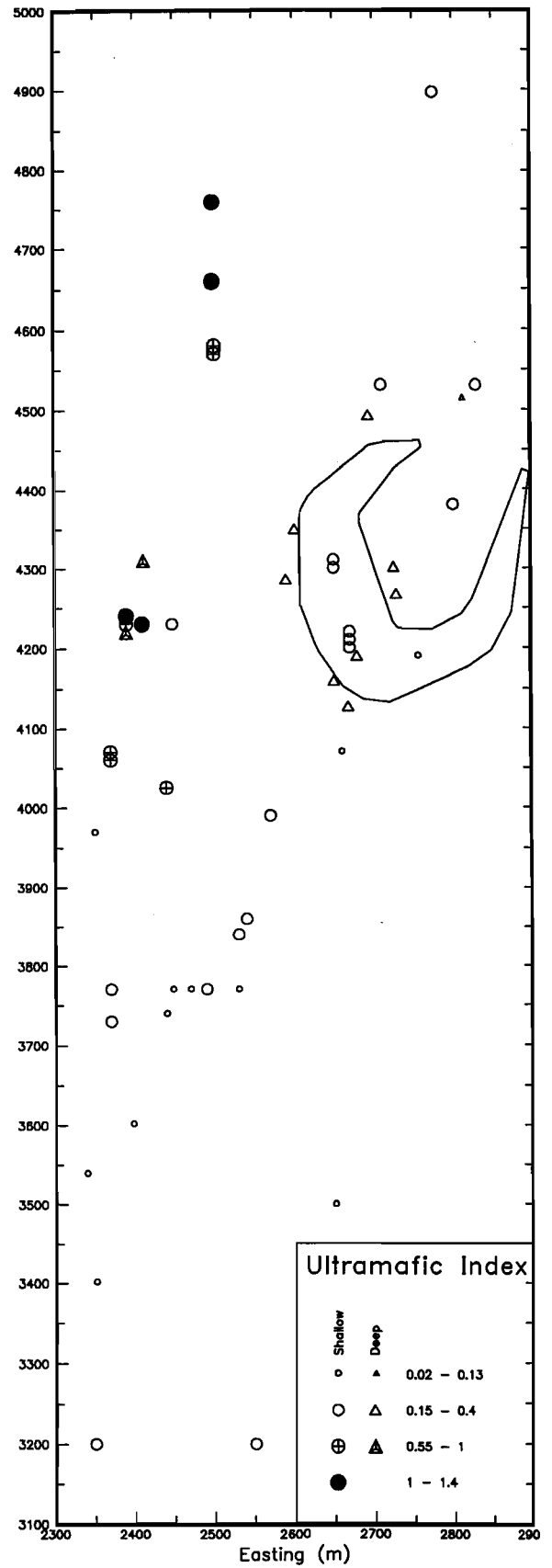


Figure 7.6: Spatial distribution of the ultramafic Index ($Ni + 2Cr$) at Panglo.

investigators (e.g., Lakin *et al.*, 1974), this mechanism was only thought to be of importance in soil solutions enriched in I by biological processes. It is possible that Au at Panglo may be more mobile than in a comparatively I-poor environment, due to the high stability of the AuI_2^- complex, relative to AuCl_2^- .

7.7 DISCUSSION

This investigation has indicated that halide transport of Au may be a major factor in supergene concentration in the Kalgoorlie area, and that dissolved Au is an adequate indicator for Au mineralization. The principal anomalies in dissolved Au occur in the northern part of the study area (Figure 7.10). These anomalies appear to be related to an intense degree of weathering in this northern region, which has resulted in enhanced redox activity (Figure 7.2), and anomalously high concentrations of Br, Mn, Co, Zn, Cu and Ni. It is hoped to continue such groundwater investigations, in order to further delineate how Au mobility, and therefore its supergene expression, is controlled by geological and/or weathering factors.

The presence of the hydrogeochemical Au anomaly at Panglo suggests that water sampling could give information on the location of buried mineralization. Separate samples would be taken for Au analysis (Report 125R) and for water quality measurements. The later sample could be sent for commercial analysis for TDS, pH and a suite of elements of interest, such as Cr, Mn, Fe, Co, Ni, Cu and Zn. Such a procedure could provide a low cost adjunct to petrological information, giving water data that could be interpreted in a manner analogous to that given above.

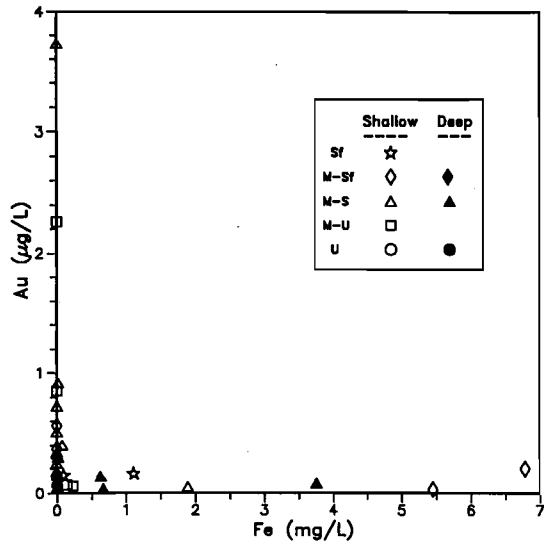


Figure 7.7: Au vs. Fe for Panglo groundwaters.

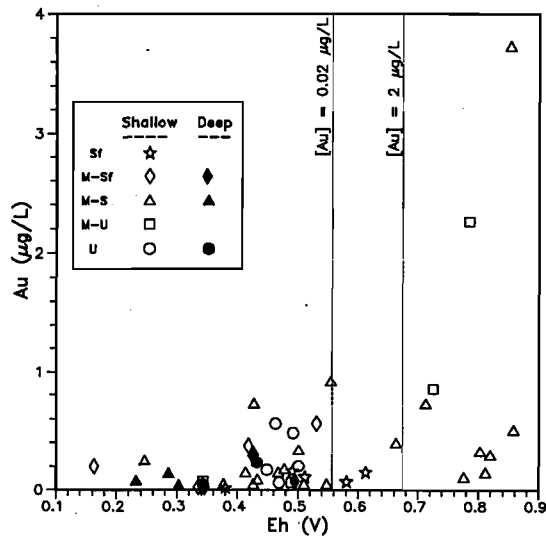


Figure 7.8: Au vs. Eh, with Eh values for dissolution of 0.02 $\mu\text{g/L}$ and 2 $\mu\text{g/L}$ Au.

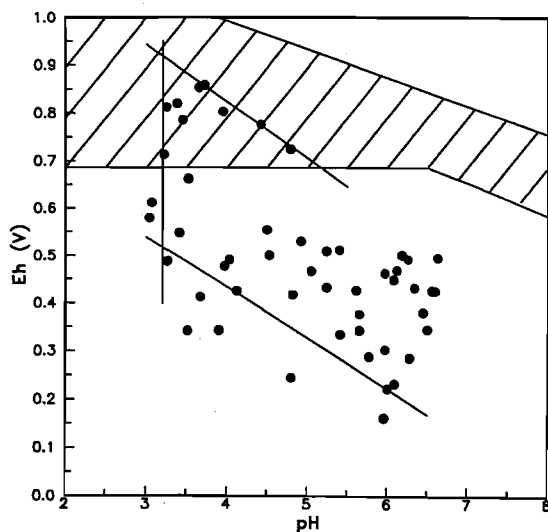


Figure 7.9: Eh vs. pH, with shaded area representing region where $[\text{Au}] > 2 \mu\text{g/L}$ with $[\text{Cl}^-] = 1\text{M}$.

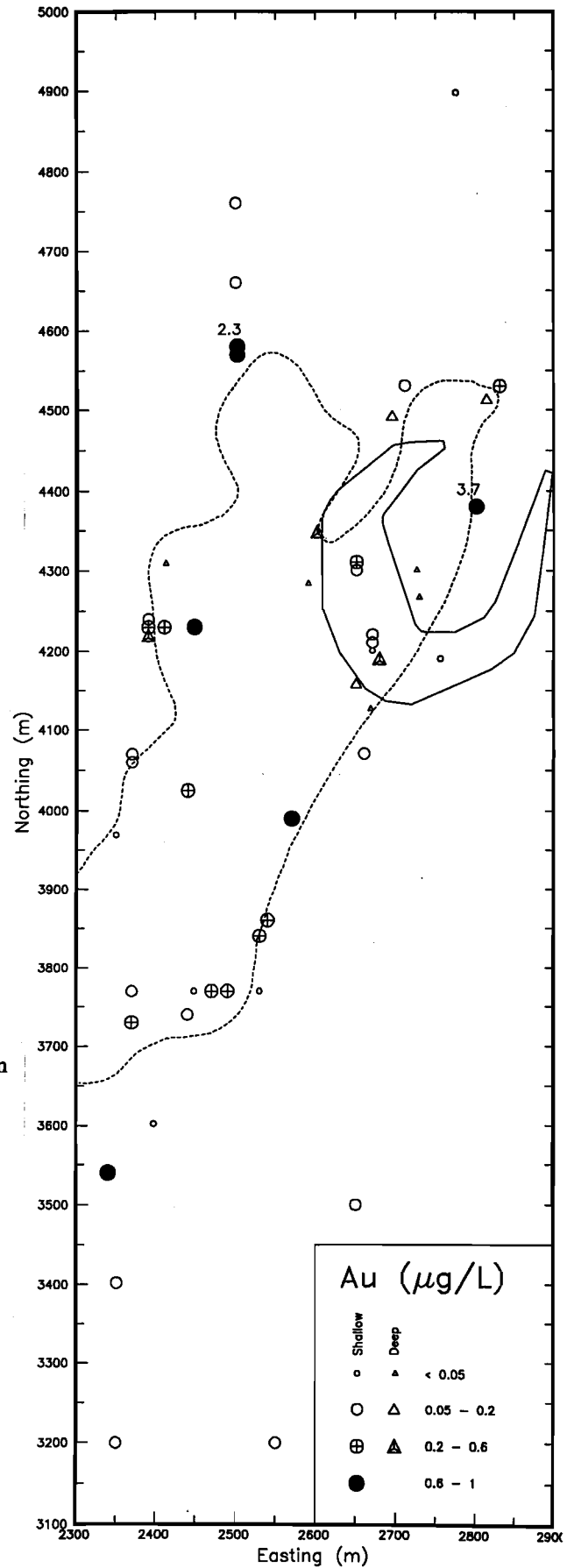


Figure 7.10: Gold concentration in water with the dashed line representing supergene expression.

8.0 RELATIONSHIP BETWEEN GOLD AND PEDOGENIC CARBONATE

8.1 INTRODUCTION

Secondary carbonates are found throughout Western Australia and are divided into two main types whose distribution is mostly defined by the Menzies Line (Butt *et al.*, 1977; see Figure 1, page iii). *Pedogenic* carbonates are an important component of the vadose zone in soils and upper parts of the ferruginous horizon in semi-arid regions of the Yilgarn Block south of the Menzies Line. *Groundwater* or *phreatic* carbonates generally form massive deposits in drainages north of the Menzies Line. The objective of this study was to investigate the nature of the association of Au with pedogenic carbonate. This association has been known for several decades, in a general sense, but little importance has been attached to it until recently. The general association has been recorded in several anecdotal accounts (e.g., Kriewaldt, 1969; K. Schulz, personal communication, 1985) and in the scientific literature (e.g., Smith and Keele, 1984; Mann, 1984a and 1989b; Lawrance, 1988a; Smith, 1987; Glasson *et al.*, 1988). Some of the early accounts (e.g., Mann, 1984) implied that the association was coincidental, and explained exclusively by physical entrapment and preservation of pieces of Au within the carbonate, i.e., a random event rather than a physico-chemical process, and this is quite clearly the case with large nuggets that have been embedded within carbonate nodules. Furthermore, during some sampling programmes, pedogenic carbonate has been actively avoided for fear that it will dilute the geochemical response, as is commonly the case for base metals (e.g., Garnett *et al.*, 1982; Guedria *et al.*, 1989). Thus, there was a need to describe and quantify the association in more detail.

The age and origin of pedogenic carbonate are important for recognizing the significance of the association with gold (e.g., Reports 159R, 129R and 24R). The regoliths and landforms of Western Australia have been developed, to a great extent, by weathering events during and since the warm and humid Tertiary period. The most pervasive example of these effects is the deep lateritic regolith found over much of the state. Since the Tertiary, the climate has become gradually drier, with evaporation far in excess of precipitation. This has led to the retention of sparingly soluble salts, in particular calcite, with the result that many soils developed from exposures of the various horizons of the lateritic regolith have become highly modified. The development of pedogenic carbonates is primarily, therefore, a function of climate. Some workers suggest that carbonate will develop in soils with rainfall less than 600 mm per annum (Young, 1976) although others suggest that calcretes in Western Australia are best developed as a function of rainfall and evaporation, e.g., 800 mm rainfall or less with mean evaporation of 1900 mm or more (Semeniuk and Searle, 1985). The effects of landform and soil type are of secondary importance. Pedogenic carbonates tend to develop in soil profiles where a gentle slope and a permeable surface are present.

8.2 SCOPE OF STUDY

Several sites were chosen to assess the significance of the association between Au and carbonate. The sites have been classified according to their geochemical landform model (Table 3.1; Butt and Zeegers, 1989). All three lateritic profile models were investigated: mostly preserved; partly truncated; fully truncated.

a. Mostly preserved; model code A1 Ca [0,1]

This regolith-landform is exemplified by Mt. Percy (Report 156R), Callion (Report 58R), and Mulline (Report 159R). At each of these sites, lateral dispersion of Au from primary mineralization has created surficial haloes characteristic of lateritic gold deposits.

The lateritic residuum at each of these sites has undergone extensive alteration by precipitation of carbonate. Carbonate occurs as coatings, veins, nodules, cements and indurated sheets and is evidently assisting in the disintegration of an otherwise resistant duricrust (eg., Plate 2.1 (a)). Iron and other major elements in the profile, e.g., Si and Al, have been diluted by later stage development of carbonate which occurs as calcite and dolomite.

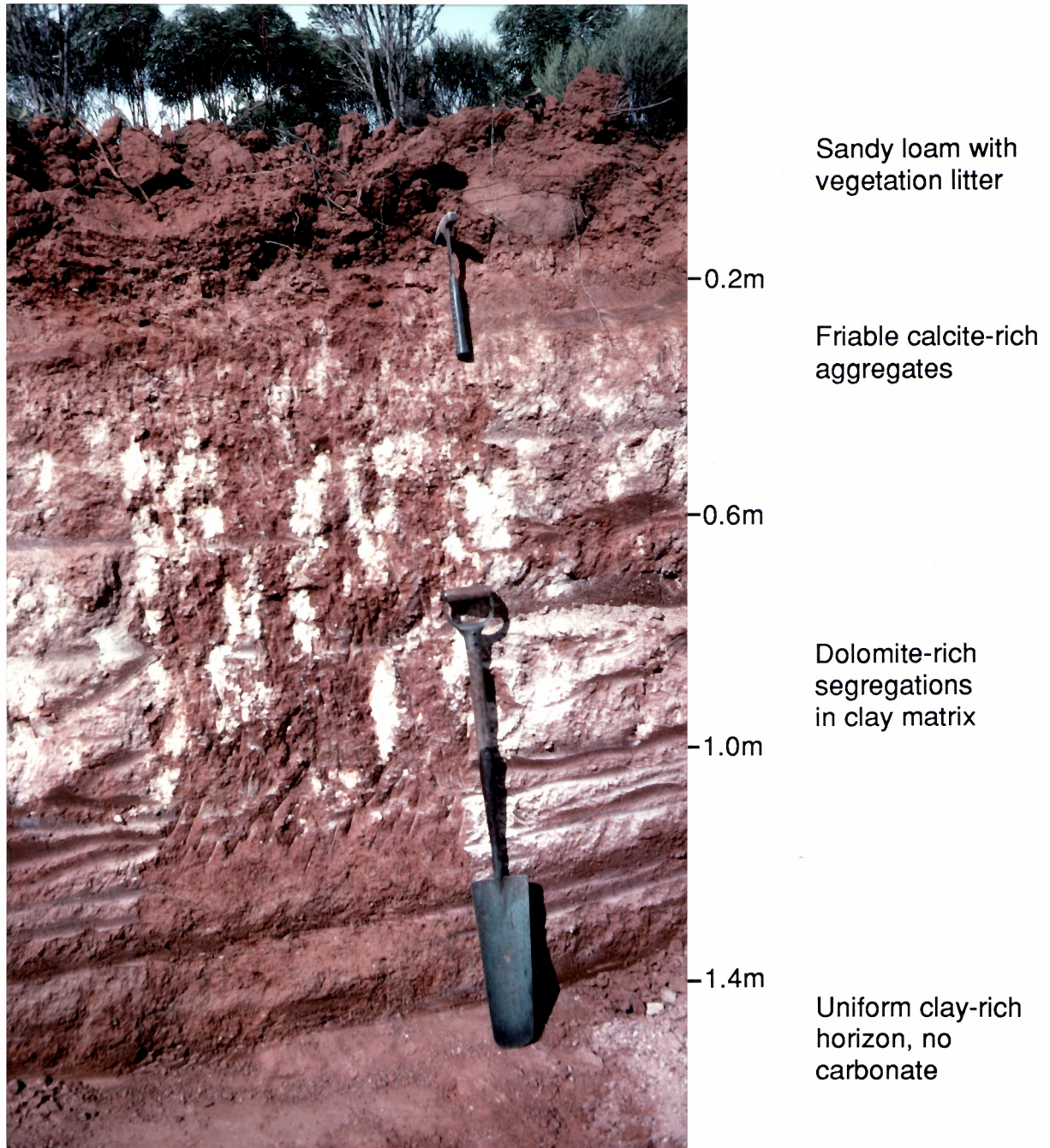


Plate 8.1 Red clay soils with pedogenic carbonate segregations, Mt. Hope. The distribution of gold closely follows those of calcium and magnesium (see Figure 8.1f).

Pre-existing Profile	A:	Mostly preserved
	B:	Partly truncated
	C:	Fully truncated
Recent alteration	0:	Minor
	1:	Low
	2:	Moderate
	3:	Strong
Recent accumulation, cementation or neoformation	0:	None
	Al:	Al-oxides
	As:	Al-silicates
	Ca:	Ca and Mg carbonates (calcrete)
	Fe:	Iron oxides
	Si:	Silica (silcrete)
Overburden on pre-existing profile	Sm:	Smectites
	0:	None
	1:	Residual soil
	2:	Semi-residual
	3:	Transported

Example: Model code B 1 Ca [1, 2] = partly truncated profile, moderate recent leaching, pedogenic carbonate, residual and semi-residual soil.

Table 8.1 Classification of models in tropically weathered terrains (after Butt and Zeegers, 1989)

Gold is present in both the Fe-rich lateritic and the Ca-rich components of the profile. It is concluded, from separate analysis of these components, that both contain Au but, in certain samples and soil profiles more Au may be associated with one particular component. At Callion and Mt. Percy, it is probable that more Au is associated with the carbonate. At Callion, Glasson *et al.* (1988) report that the highest concentrations (16 ppm Au over 5 m) occur in the carbonate, compared with adjacent carbonate-poor sections (e.g., 6 and 4 ppm over 5 m).

The location of Au in the soil appears to be determined by the relative proportions of the lateritic and calcareous components with which it is found. Understanding of the distribution of the Au must take the two components into account. In general, the addition of pedogenic carbonate to a soil horizon dilutes the abundance of other, pre-existing components. At Mulline (Report 159R), this feature is observable, for example, in the distributions of Fe and trace elements, (including Au) contained within the lateritic Fe oxides. In contrast, the abundances of elements associated with the carbonates (e.g., Ca, Mg, Sr) are increased. For Au, however, the accumulation in the carbonate horizon generally offsets the dilution of the Au associated with Fe oxides, such that there is a net increase in Au abundance. Accordingly, there is no simple correlation between the abundance of Au with either Fe or Ca.

b(i). Partly truncated, semi-residual; model code B1 Ca [1, 2]

The association of Au with pedogenic carbonate within saprolite was studied at Mt. Hope (Reports 24R and 109R) and at Panglo (Report 129R). The lateritic cover is locally preserved either at surface or buried by transported clays. However, partly colluvial and partly residual clays, derived from saprolite, are more abundant over mineralized areas and in the broad valleys. In places, residual, lateritic residuum present over mineralization contains some Au but, unlike Callion, Mt. Percy and Mulline, it commonly does not contain appreciable amounts of carbonate i.e., it belongs to A1 0 [0] model.

In the areas where the lateritic profile has been truncated, pedogenic carbonate has developed extensively within the clay-rich surficial material down to 1-2 m. It has a dominantly powdery texture and occurs as coatings on fine soil clay- and silt-sized particles and as veins, partings and coating fractures (Plate 8.1). Dismantling and replacement of the indurated saprolite by carbonate was evident from SEM studies and field observations (Report 129R).

The concentrations of Ca, Mg and Au are closely correlated (Figure 8.1). Their abundances generally increase steadily from the surface and reach a maximum within the top metre and then declines with little present below two metres. Carbonate-rich profiles are dominated either by calcite or dolomite; those containing dolomite commonly have a less well-developed horizon of calcite present above, which merges with the dolomite horizon. The relationship is also evident in traverses across mineralization, where soils having different carbonate content are compared (Figure 8.2). Where traverses extend into unmineralized areas, the Au:carbonate ratio declines over a short distance (Report 109R).

Elongate powdery segregations of carbonate often occur within profiles and appear to be have infilled old root channels. If the analyses of the carbonate segregations are compared with those of adjacent material of low carbonate content, the association between gold and carbonate is poor (Table 8.2). This suggests that carbonate itself is not intrinsically important for Au precipitation and that the association is indirect (see Sections 8.4, 9.2 and 9.3). In addition, minor amounts of Au are present in Ca-poor, preserved lateritic material where it appears to be associated with Fe.

b(ii). Partly truncated in situ; model code B1 Ca [1,2]

At Panglo, the lateritic residuum has been stripped to reveal a residual saprolitic clay over much of the mineralized area. This is locally strongly indurated. Carbonate is abundant in the top metre of the profile. It occurs as fine coatings on the clay material. Where the saprolite is ferruginous and indurated, the carbonate occurs as veins and cements similar to the situation with preserved lateritic material at Mulline.

There is a strong association between gold and carbonate within the soil profile. This is evident from analytical data of the traverse across supergene mineralization in soils (0-10 cm) having differing carbonate contents (expressed as CaO and MgO, Figure 8.3). Detailed analysis of carbonate coatings, cements and the host indurated saprolitic material for Au also demonstrate this association (Table 8.3). Gold is also present in some Ca-poor surficial material where it appears to be associated with partly-weathered primary material (lithorelicts).

c(i) Partly truncated, transported; model code B 1 Ca [3]

Sediment-filled palaeochannels are widespread but subdued features of the landscape of the Yilgarn Block that may contain Au (e.g., as "deep leads") or overlie Au mineralization. Such a channel crosses the southern part of the mineralized zone at Panglo. The sediments consist of up to 3 m of loosely-cemented, Fe-rich gravels and fragments of part-weathered to fresh country rock overlying 7-10 m of silty clay. A trench on the margin of the channel shows that pedogenic carbonates have been precipitated in the top metre of the sediments and occur as occasional nodules and aggregates (to 10 mm), smaller aggregates (<3 mm), thin coatings (<1 mm) and fine powder. Calcite is the dominant mineral. The total Fe content of the first metre is strongly diluted by the presence of the carbonate.

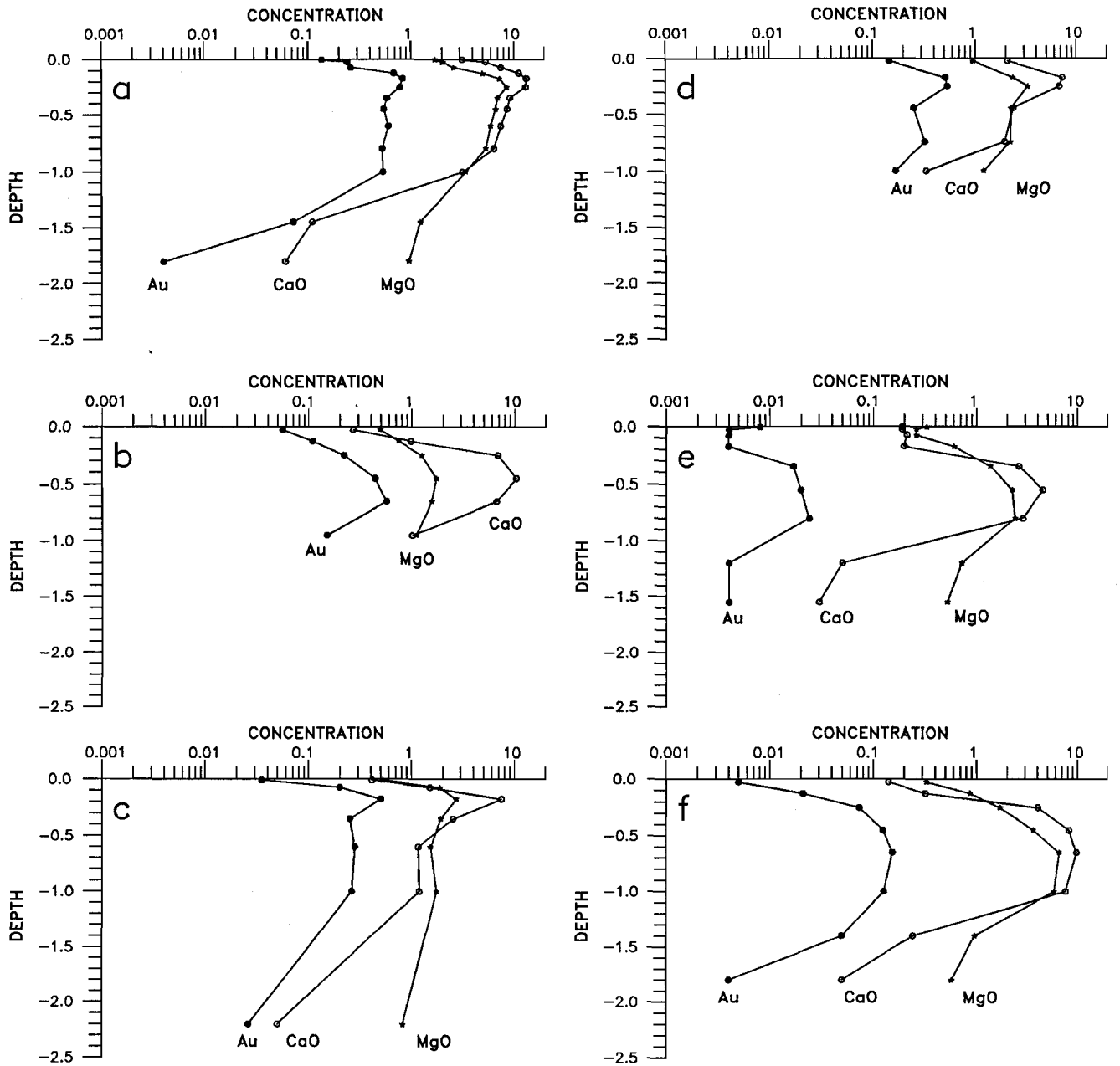


Figure 8.1: Depth profiles for CaO, MgO and Au in carbonate-rich soils: a) pit 1; b) pit 4; c) pit 5b; d) pit 5a; e) pit 6; f) pit 7 (Mt. Hope, Report 24R). The profile in pit 7 (f) is shown in plate 8.1.

Table 8.2: Compositions of whole calcareous soil samples and their separate ferruginous and calcareous fractions, Bounty Zone, Mt. Hope.

Sample	Au ppb	Fe ₂ O ₃ %	CaO %	SiO ₂ %	Al ₂ O ₃ %	MgO %
04-1205						
Whole soil	830	3.9	13.2	42.2	7.7	7.3
Ferruginous	962	4.1	10.9	48.2	6.7	6.4
Calcareous	1070	3.4	15.7	34.7	9.1	9.2
04-1211						
Whole soil	530	5.4	3.2	63.4	13.2	3.4
Ferruginous	512	5.7	2.1	65.4	13.4	2.2
Calcareous	590	5.0	5.1	58.5	11.9	4.0
04-1212						
Whole soil	72	4.0	0.1	70.9	14.0	1.2
Ferruginous	122	4.2	0.1	71.7	14.0	1.0
Calcareous	122	5.0	1.4	68.4	10.5	1.6
04-1292						
Whole soil	-	-	-	-	-	-
Ferruginous	188	4.6	5.4	62.5	12.5	2.6
Calcareous	134	3.3	15.3	38.0	8.4	8.5

Gold mineralization is distributed within three main zones within the regolith: (a) enrichments (50-1000 ppb) intimately associated with the pedogenic carbonate horizon (Figure 8.4); (b) minor enrichments (< 1 ppm) at the unconformity at the base of the palaeochannel at about 12 m depth, possibly related to a palaeosol; economic grades of gold (> 3 ppm) as a supergene deposit at about 40 m. The surficial Au enrichment occurs directly above the Au enrichment at the unconformity and this, in turn, over the supergene mineralization. In addition, some lateral dispersion of gold has taken place at the surface.

Of particular note at Panglo is that channel sampling at a set height from the *bottom* of the trench did not define the boundary of supergene mineralization, but, instead, the anomaly was displaced to one side. This is because the carbonate horizon (which contained the Au) was only sampled where the trench was shallow. The deeper parts of the trench were sampled below the carbonate horizon and, therefore, missed the Au enrichment. Augering, sampling and compositing the first metre, on the other hand, correctly located supergene mineralization since it consistently sampled the carbonate horizon, situated in the first metre (Figure 8.5). Clearly, consistently sampling of the correct horizon is important for obtaining meaningful data and performing correct interpretation.

c(ii) Fully truncated, transported; model code C 0 Ca [3]

At Mt. Pleasant, carbonate is developed in the first metre of colluvial sediments. The sediments are up to 5 m thick and are located directly on the partly weathered rock. Little or no development of saprolite is evident. Gold appears to be present within the carbonate horizon (Lawrance, 1988a) and gives a subtle surface expression of otherwise concealed mineralization (Figure 4.6).

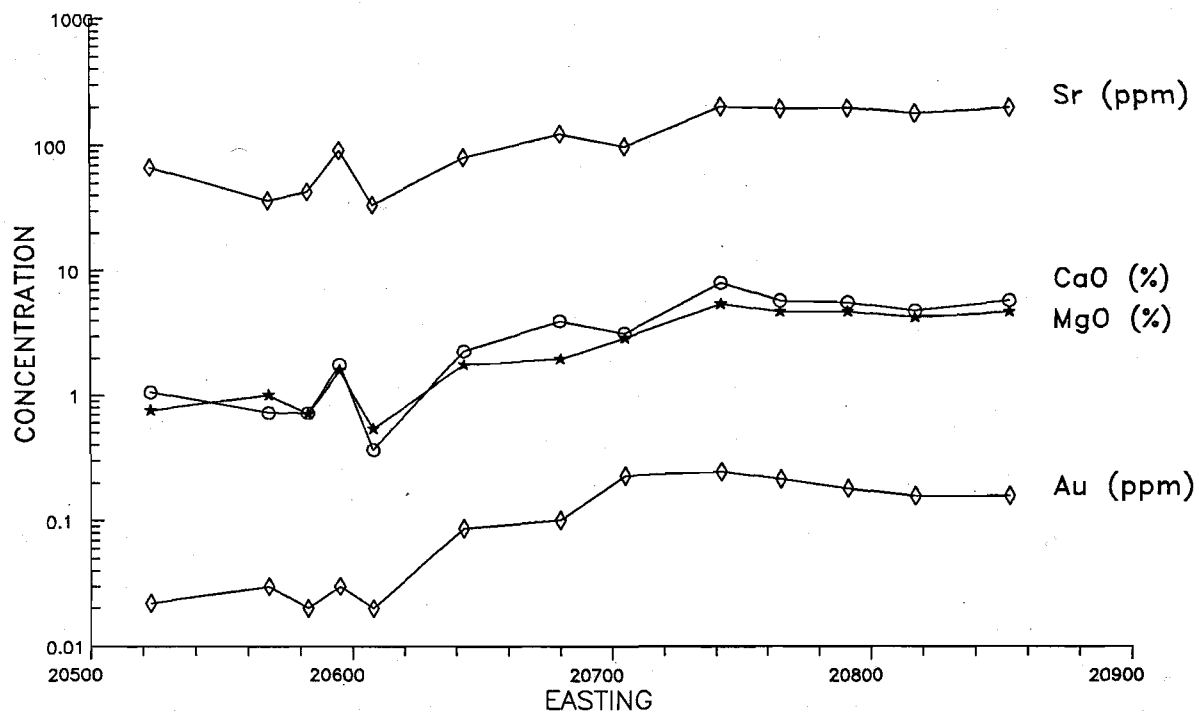


Figure 8.2: Distributions of Au, CaO, MgO and Sr shown by sampling 0-1 composite samples, traverse 35800N, Mt. Hope.

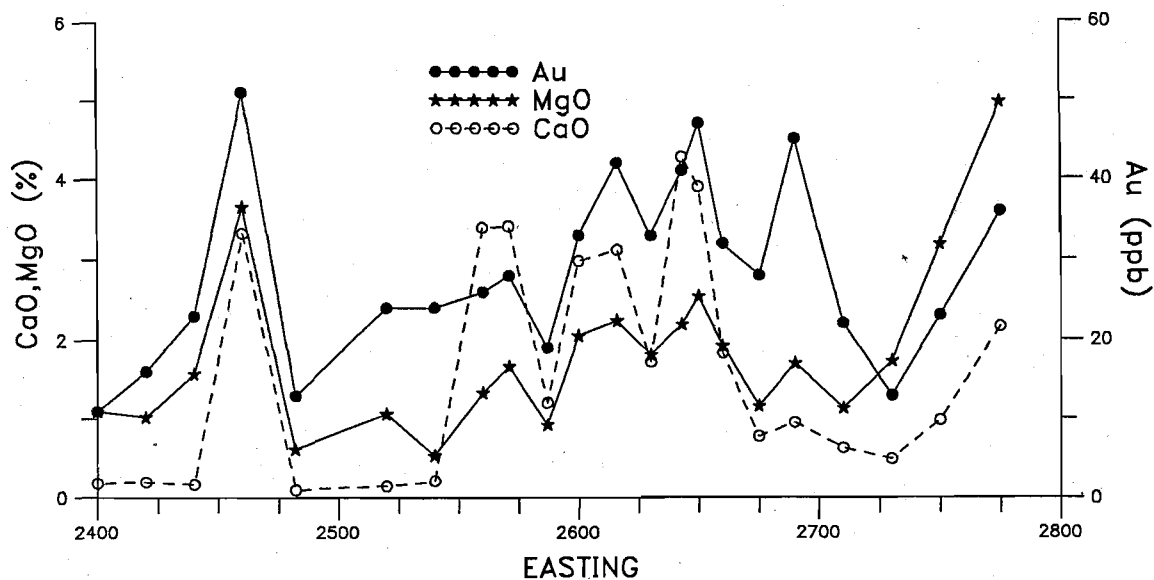


Figure 8.3: Distributions of Au, MgO and CaO shown by sampling surficial soil 6-20 cm, traverse 4200N, Panglo.

Table 8.3. Compositions of whole samples and hand separated fractions from carbonate-coated saprolite, Panglo.

Sample	Type	Au ppb	Fe ₂ O ₃ %	CaO %	SiO ₂ %	Al ₂ O ₃ %	MgO %
04-2129	Whole sample	267	3.7	2.1	36.6	11.3	0.4
04-2150	Carbonate	62	1.0	39.5	11.4	2.2	3.9
04-2153	Carbonate	157	1.9	36.8	11.7	2.2	2.9
04-2154	Carbonate	210	4.1	32.1	18.9	3.4	3.4
04-2156	Carbonate	173	3.3	33.2	18.6	3.2	3.4
04-2157	Carbonate	199	2.6	33.1	17.8	3.4	3.5
04-2151	Pale saprolite	<2	0.6	6.7	60.3	16.7	0.7
04-2152	Red saprolite	<2	28.7	0.2	43.7	12.3	0.2
04-2155	Red saprolite	2	32.5	0.4	37.0	12.9	0.5
04-2158	Red saprolite	12	33.6	0.4	34.6	12.6	0.5

8.3 SOURCE OF ALKALINE EARTH METALS

The close association of carbonate and gold underline the significance of carbonate as a sample medium. The major carbonate minerals identified in the study areas are calcite and dolomite. Calcium is an essential component to both minerals although many of the sources described will be common to Mg (and Sr). Calcium can be introduced into soil from many sources (Dregne, 1976):

- 1) From the underlying rock: by chemical or physical weathering of Ca-bearing rocks and saprolite found within the soil e.g., amphibolites or limestone.
- 2) From biogenic sources: by biological break-down of Ca-bearing animal and plant residues e.g., bones, leaf and bark litter, branches, trunks and roots or leaf exudates.
- 3) From atmospheric sources: by rainfall, aerosol or wind-blown dust (e.g., from salt lakes, or limestone from the Nullarbor Plain).
- 4) From groundwater sources: by capillarity or inundation from a Ca-bearing groundwater in a shallow or near-surface saturated zone.

As discussed below, the first three of these sources are probably the most important in the areas studied and essentially rely on their interaction with the movement and chemical properties of soil water for formation i.e., they are pedogenic. In the Yilgarn Block, the most immediate sources of Ca and Mg are mafic and ultramafic rocks, respectively. On weathering, these parent materials are altered to ferruginous laterite at surface and saprolite at depth. The rock from which they were derived is generally found at considerable depth. However, despite being highly leached, the saprolite can still contain small, but significant, amounts of Ca (e.g., several hundred ppm, Report 156R). Atmospheric sources contribute significant amounts of Ca to the

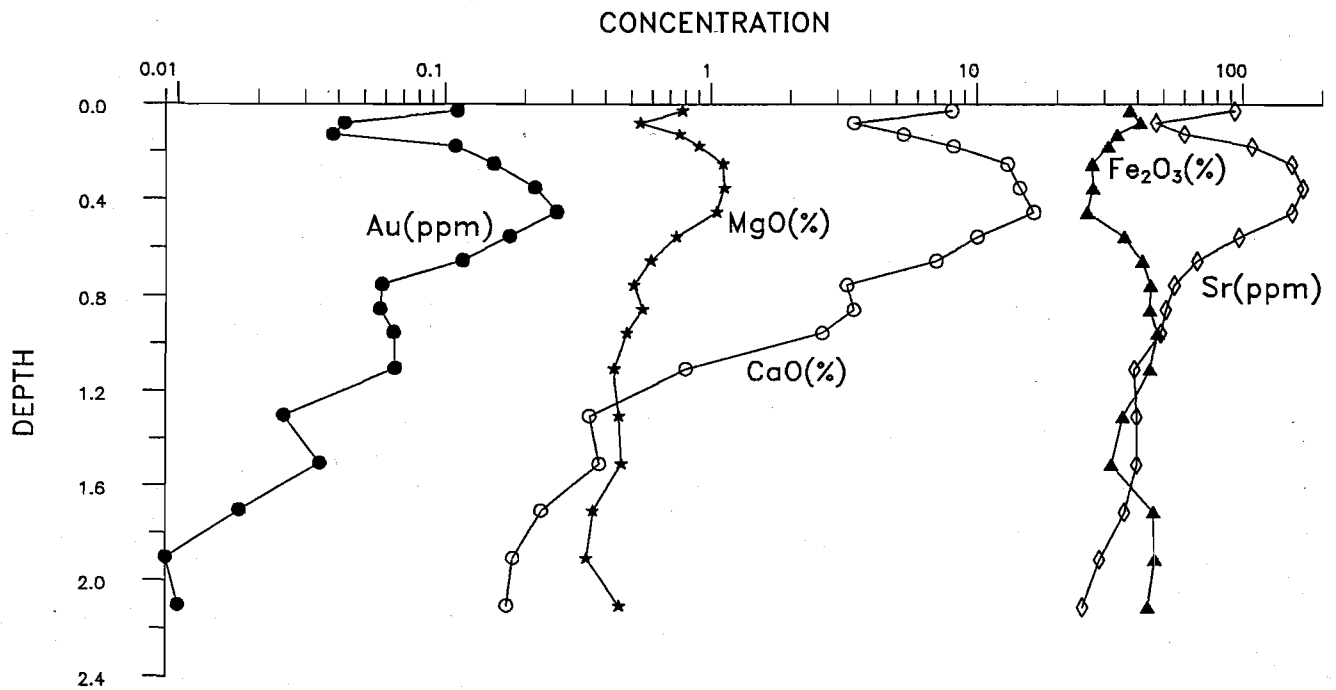


Figure 8.4: Depth profiles for CaO, MgO, Sr, Fe₂O₃ and Au in a carbonate-rich soil profile at Panglo (Report 129R).

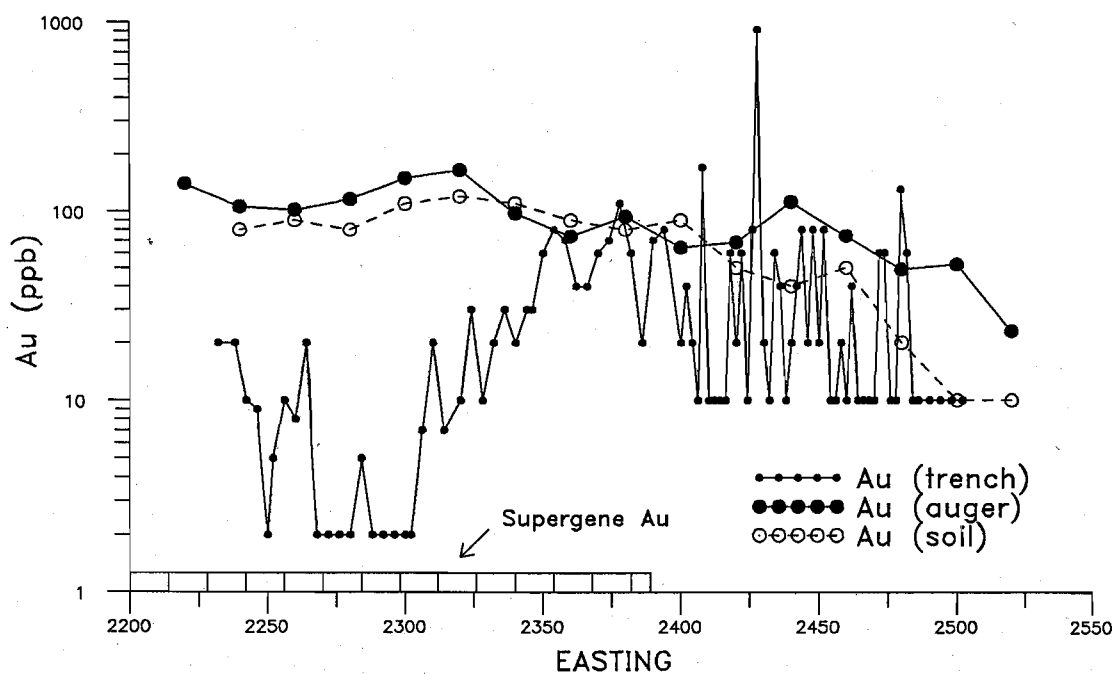


Figure 8.5: Comparison of Au data for auger (0-1.2 m), soil (0-20 cm) and trench sampling (about 0.5 m from base of trench) at Panglo (Report 129R).

soil of Western Australia in the form of dust and rainfall (Hingston and Gailitis, 1976). From their data, it is estimated that about 1-2 kg of Ca per square metre (as carbonate equivalent) fall on Kalgoorlie every 1000 years. This figure increases considerably in other areas closer to source materials such as salt lakes, the ocean or the Nullarbor Plain. Vegetation plays a major role by bringing Ca to the surface from the deeper regolith as well as by re-working of Ca that is already in the soil (Reports 24R and 129R). Thus, it is likely that there is no unique source of the soil Ca but rather it is derived from a combination of several sources. In addition, some Ca will have been transported and/or re-worked by external water e.g., run-off and lateral or vertical sub-surface flow. Groundwater does not play a direct role in the present day accumulation of Ca in the study areas. Capillarity (the mechanism by which groundwater can travel upwards by surface tension against gravity) is only effective over 1-2 m (McFarlane, 1976) whereas the shallowest water-table (at Panglo) is at about 5-10 m depth and at Mt. Hope it is at about 90 m depth. This does not entirely preclude the possibility of groundwater being an important source of alkaline earth metals in the past when rainfall was higher and water-tables may have been closer to the surface; however the widespread nature of carbonates throughout the landscape and their conformity with the present landsurface makes this origin improbable. Groundwater or non-pedogenic carbonates have typically formed in valleys. In WA, these are particularly common north of the Menzies Line (Butt *et al.*, 1977) and were not considered in this study.

8.4 MECHANISM OF PEDOGENIC CARBONATE FORMATION

Dolomite and calcite form in the soil by the interaction of Ca^{2+} , Mg^{2+} and CO_3^{2-} . The origin of CO_3^{2-} is probably attributable to CO_2 gas produced by root and microbial respiration. Production of CO_2 will be greatest slightly below the surface, where organic material from vegetation will be degraded, and in the root zone (rhizosphere), typically within the first metre of the soil. Some CO_3^{2-} may be derived from bicarbonate-enriched, near-surface groundwaters, but this mechanism does not apply in the study areas under the present climatic regime, as discussed above.

Carbon dioxide dissolves readily in water and dissociates to the bicarbonate ion (HCO_3^-) which, in turn, reacts with free Ca^{2+} to deposit calcite. The concentration of Ca^{2+} is dependent on the partial pressure (gas concentration) of CO_2 , the pH and temperature. Thus, as CO_2 is produced by respiration and is dissolved in downwards-percolating meteoric water during the wet season, freshly precipitated calcite will re-dissolve. Precipitation will occur as saturation with respect to calcite is reached, through a reduction in temperature, through water being removed by evapotranspiration or by an increase in pH. The depth to which this process will continue will depend on soil permeability, slope and the frequency and volume of rainfall. The wetter the soil, the deeper the Ca will move into the profile. In semi-arid or arid soils, the removal of water by evapotranspiration is likely to be the major controlling factor. The process of dissolution and re-precipitation of calcite will continue until the soil environment changes for an extended period e.g., during the dry season. Over many seasons and, with a soil that has an open-spaced pore structure (e.g., clay-rich), a Gaussian normal depth distribution of carbonate would be expected to form in the soil profile with a maximum concentration and thickness that reflects an averaging of these soil conditions over many years. This appears to be the case in the first two metres of many soils at Panglo and Mt. Hope (Reports 24R and 129R). However, for indurated soil horizons with an irregular structure of large pores (e.g., lateritic residuum), although the total amount of carbonate may be similar in the first two metres to that found in clay-rich soils, it may be preferentially distributed as partings, coatings and cements. This occurs in some profiles at Panglo, Mt. Percy and Mulline (Reports 129R, 156R and 159R). Further evidence for this mechanism is found in the structures of some of the powdery carbonates and rhizomorphs, which strongly suggest they have formed recently. The presence of dolomite beneath calcite in many of the soil profiles at Mt. Hope (Report 24R) suggests that Ca and Mg have originated from the surface. Calcite precipitates from soil solution before, and hence above, dolomite in soil profiles; dolomite forms comparatively slowly in the surficial environment (Drever, 1982); this phenomenon has been observed in soils in South Australia (Wetherby and Oades, 1975).

8.5 MECHANISM OF GOLD CARBONATE ASSOCIATION

The Au distribution within soil profiles closely follows that of Ca, so it is not unreasonable to assume that Au is controlled by a similar sequential process i.e., it is likely to be precipitated by the removal of water from the soil, and then re-mobilized with the addition of water. Precipitation at a pH barrier is improbable, for this would result in a Au-enriched zone at the top or bottom (depending on the source) of the carbonate horizon. Field and laboratory observations from this study and elsewhere (Ong and Swanson, 1969; Lakin *et al.*, 1974; Smith and Keele, 1984) suggest the role of vegetation is important for the distribution of Au in soils; for example, (i) the presence of Au (>0.3 ppm in ashed material) and Ca (generally $>20\%$ in ashed material) in vegetation (Reports 24R and 129R), (ii) the presence of Au in transported material above mineralization (Report 129R) and (iii) the highly soluble nature of Au in soil material found in laboratory studies (Report 126R). The presence of Au and Ca in plant material demonstrates the role of vegetation in the mobility and dispersion of these elements and suggest not only that the Ca-Au association is at least partly biogenic, but also provides an explanation for the enrichment of Au in soils (Figure 8.6). It is difficult to explain the origin of Au in the soils developed over the palaeochannel at Panglo unless Au is derived from below the transported material via deep-rooted plant species e.g., *Eucalyptus* spp., (Report 129R). At the surface, Au can be absorbed via shallow-rooted plant species e.g., *Melaleuca* spp. shrubs, (Report 24R) by interacting with soluble organic matter; this process may explain the apparent mobility of Au in the soil profile by preventing precipitation as Au metal by forming a protective colloid or sol (Reports 126R and 128R). Only where transported material is not a major regolith component, and there is no surficial depletion zone so that Au derived from primary mineralization extends into the soil, can hydromorphic dispersion of surficial Au, interacting with organic matter, be the most important dispersion mechanism. The contribution from Au re-mobilized through the vegetation is then only minor. The mechanisms of gold mobility in soil are discussed more fully in Section 9.0.

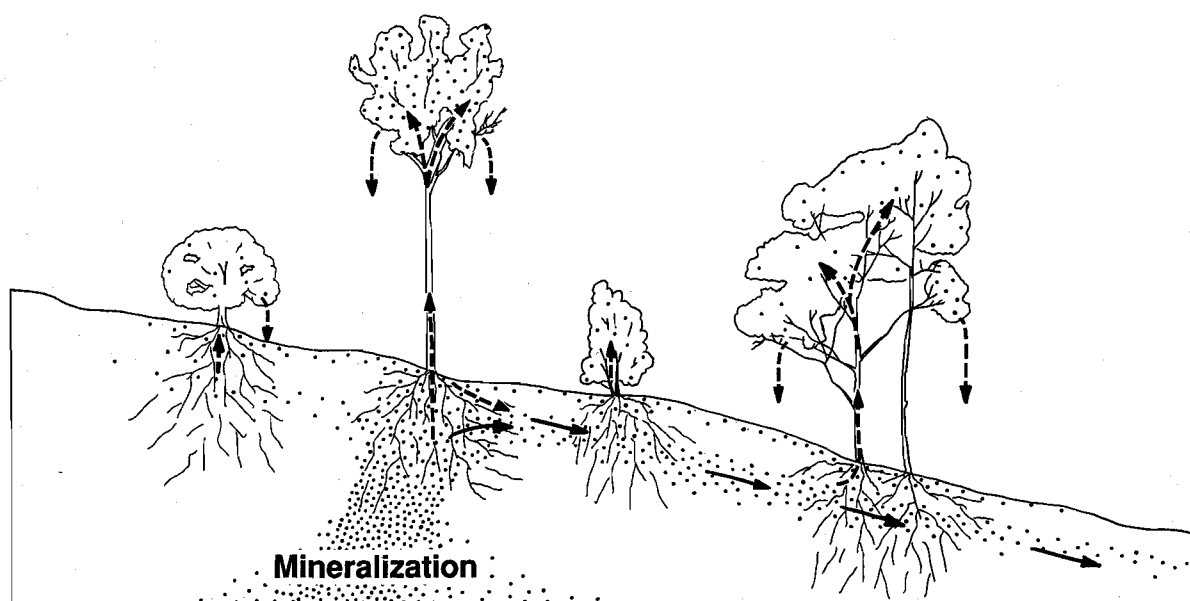


Figure 8.6: Schematic dispersion pattern of Au (dots) via the vegetation (broken arrows) and solely within the soil (solid arrows).

8.6 IMPLICATIONS FOR EXPLORATION

The study suggests that:

- (i) the carbonate horizon should be identified in the field (e.g., by using dilute HCl), sampled and logged;
- (ii) gold anomalies may not be exclusively confined to carbonate material but may also be within lateritic gravels and duricrusts. These should be sampled separately and logged;
- (iii) clear associations between pathfinder elements and mineral phases, excluding Au, are difficult to recognize, because of the effects of dilution by secondary carbonate;
- (iv) the pedogenic carbonate horizon is usually confined to the top metre of the soil profile;
- (v) some surficial carbonate forms (e.g., powdery) may contain more Au than other forms.

The results strongly suggest that Au is associated with the soil carbonate. The carbonate horizon may vary with depth but generally occurs within the top metre. Where exploration techniques use the association of Au with carbonate, the location and presence of carbonate within the soil profile must be noted. A surficial soil sampling programme, although being a relatively inexpensive option in terms of collection, may be costly if it fails to sample the carbonate and miss a soil anomaly and potential gold deposit. Routine, deep RAB drilling is effective for all types of material, including the carbonate horizon, but is more costly. The most cost-effective procedure by which the carbonate horizon can be sampled is by shallow auger drilling. This has the capability of sampling at greater depth if the carbonate horizon occurs below one metre. The expense of power-auger drilling is clearly greater than surficial soil sampling but it is justified because, unless the correct horizon is sampled, Au anomalies may be overlooked.

Pedogenic carbonate formation is just one process currently active in semi-arid and arid areas of WA. Many other processes, including clay illuviation, silicification and salinization have taken or are taking place. In areas close to or north of the Menzies line, pedogenic carbonates are only patchily developed or absent and the concentrations of gold in soil become locally variable and very low. The mechanisms of gold dispersion under present conditions in these areas warrants investigation. In addition, groundwater-derived carbonates, for example, have not been studied as a possible source of secondary enrichment for Au, although they are well known for their capacity to host uranium mineralization.

9.0 CHEMISTRY OF GOLD IN SOILS

9.1 INTRODUCTION

Soil sampling is extensively employed in modern-day Au exploration. An important part of the Project has been to examine the distribution of Au in soils, to improve soil sampling and interpretation techniques. However, although much is known about the chemistry of Au, both in the laboratory and the aqueous weathering environment (Report 4R), its chemistry and mobility in soils are generally poorly understood. Soils contain phases such as organic matter, amorphous Fe oxides or fine clays that are difficult to characterize and have very complex interactions with metals. Various chemical techniques (such as selective extractions) have been devised in order to understand these interactions and techniques have become widely used. However, Au presents particular problems, due to its tendency to chemical reduction and its high reactivity with many of the reagents used in soil investigations. Therefore, it has been necessary to devise specific techniques to investigate the chemistry of Au in soils, as described in Reports 126R and 127R. In addition, work has been done to continue previous research on the chemistry of the interactions between Au and soluble humic matter (Report 128R). This section briefly describes the results from these reports.

9.2 CHEMISTRY AND BIOGEOCHEMISTRY OF GOLD IN SOILS

9.2.1. Soil materials

Samples from three soil profiles (A, B and C) were selected from the Mt. Hope gold deposit. These profiles contain several hundred ppb Au and are examples of two common soils occurring throughout the southern, semi-arid part of the Yilgarn block (Report 126R). The profiles are of a red clay soil consisting of kaolinite clay infused near the surface with pedogenic carbonate (Profiles A and B), and a sandy gravelly soil, with ferruginous lateritic nodules, that contains very little carbonate (Profile C). The close association of Au with pedogenic carbonate, as in Profiles A and B, has been observed in many locations in the southern Yilgarn block (Section 8).

Three samples were taken from Profile A for extensive study. Samples 1467 and 1468 were taken close to the surface (5-15 and 15-25 cm, respectively), and have high to moderate levels of organic matter. Sample 1470 was taken from 60-80 cm and is rich in carbonate, with little organic matter. The characteristics of samples from Profiles B and C are detailed in Report 126R, Section 2.

9.2.2. Selective extraction

Initial solubility tests were done using water, $\text{S}_2\text{O}_3^{2-}$, SCN^- , OH^- (taking the soil-water mixture to pH 10), I^- and CN^- , thus representing a range of extractive strengths (Report 126R). Gold in soils was commonly found to have a high solubility, implying it to be present as very finely divided particles, sorbed ionic Au, or as other types of "chemical Au". As expected, water alone is very poor at dissolving Au in the short term, whereas $\text{S}_2\text{O}_3^{2-}$ and SCN^- appeared to extract Au from many soils. Water at pH 10 (OH^-) extracted up to 20% of the Au from organic-rich samples, with minimal dissolution from other samples. This effect may be due to OH^- dissolving a normally insoluble Au compound, such as an organic complex. The I^- reagent differed markedly from the other reagents in that it particularly extracted Au from carbonate soils and some lateritic materials, whereas CN^- extracted Au too rapidly, even when diluted and unbuffered (Report 126R; Section 6.2), to give useful solubility data.

On the basis of these tests, I^- was chosen as the most effective reagent for investigating the chemistry of Au, using samples from Profiles B and C. The extractions were done on samples that were merely crushed to < 10 mm, and samples that were pulverized to < 75 μm , in order to test for any effect of occluded Au.

In Profile C (carbonate-poor), CN^- and I^- extractable Au were generally lower when the samples were crushed rather than pulverized, as expected, due to occlusion effects. The deeper part of Profile C (which is richer in

Au) corresponds with the zone where Au is least extractable by I^- . High values of I^- extractable Au were observed in the uppermost organic-rich zone, probably due to dissolution of Au associated with organic matter.

The extraction of Au from pulverized samples from Profile B (Figure 9.1b) was moderately effective (10 - 30% of the total Au) by I^- . Less Au was extracted by CN^- from crushed samples than pulverized (Figure 9.1a). However, I^- extractable Au was generally higher in the crushed samples than in the pulverized samples, except in the organic-rich samples (similar to the organic-rich zone of Profile C).

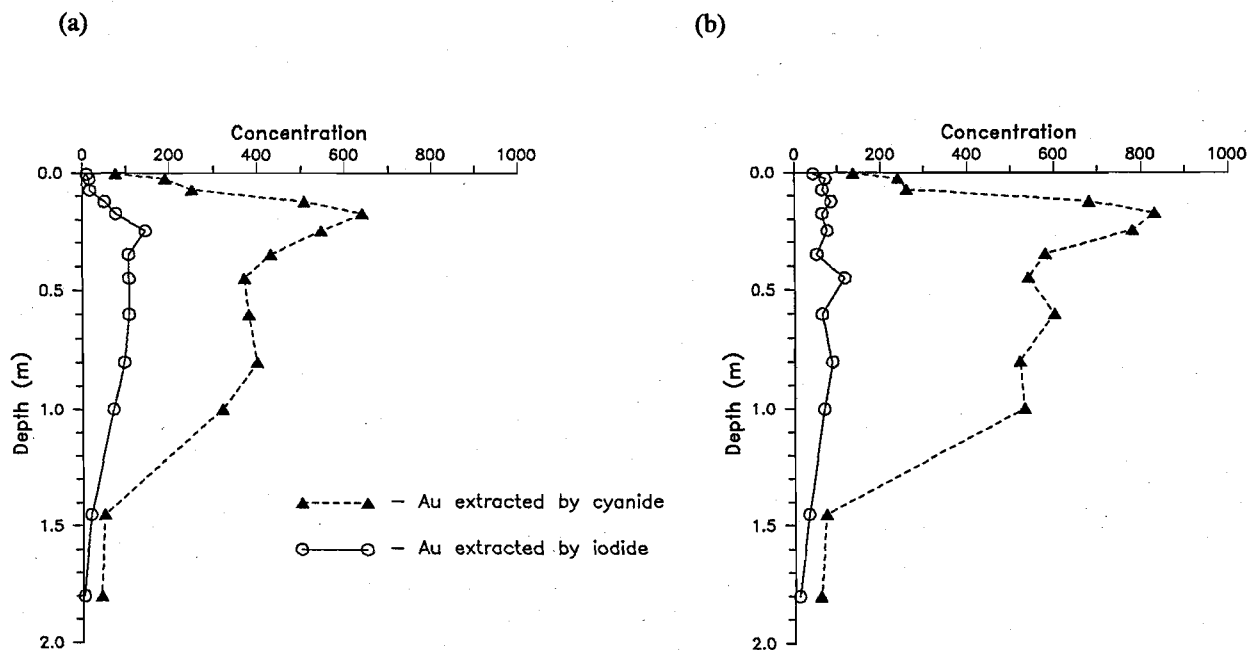


Figure 9.1: Gold extracted by various reagents versus depth, using (a) crushed (< 10 mm), and (b) pulverized (< 75 μ m) samples from Profile B.

Because Au is concentrated in carbonate horizons, it was expected to be firmly bound. However, the results suggest the opposite, namely that Au associated with the carbonate is *more* chemically extractable than in the upper organic-rich zone or in the deeper carbonate-poor zone, and that a significant proportion of the Au associated with the carbonate is present in a form that is readily accessible to the solution.

The extraction experiments suggest that Au may exist in a number of different forms:

- (i) Associated with organic matter in the upper part of the soil. This Au is particularly extractable when the soil material is pulverized, suggesting that the Au is occluded.
- (ii) Associated with the Fe oxides or other, non-carbonate material. This Au has a moderate extractability in I^- , which is considerably lowered for the samples that are merely crushed, suggesting that the Au occurs within solid phases.
- (iii) Associated with carbonates. This Au is strongly extracted by I^- solutions, particularly in crushed samples, suggesting that a substantial part of the Au is on surfaces or in environments that are readily accessible to the solution.

9.2.3. Soil incubations

Samples were investigated by batch experiments (Report 126R; Section 3) by the addition of deionized water to soil, followed by shaking and sampling of bottles at varying intervals. Parallel experiments were also run, involving bubbling with CO_2 (so as to simulate the high CO_2 environment of soils), irradiation (to sterilize the mixtures), and irradiation followed by later 'inoculation' with small amounts of non-irradiated soil. An additional set of parallel experiments were done, in which the mixtures were spiked with Au.

Analyses of solutions collected over a six month period implied specific controls over the soil - solution interactions:

- (i) the very low rate of dissolution of calcite and Fe oxide, and the observed dissolution of dolomite could be due to dolomite and other late-stage precipitates occluding the other soil minerals ;
- (ii) dissolved HCO_3^- , Ca, Mg, and K contents increased significantly over time, presumably due to carbonate dissolution in response to acid production from oxidation of organic matter;
- (iii) the readily soluble ions Na^+ , K^+ , Cl^- , Br^- , SO_4^{2-} and NO_3^- showed much higher concentrations in mixtures of the carbonate-rich samples, suggesting that it represents an evaporative zone. In contrast, solutions of the carbonate-poor Profile C were 10 to 50 times less saline;
- (iv) Br^- and I^- concentrations increased over time, presumably due to organic matter decomposition;
- (v) bubbling with CO_2 induced anaerobic conditions, and in organic solutions all of the SO_4^{2-} was lost, presumably via reduction, whereas in carbonate-rich samples, which had less initial organic matter and more SO_4^{2-} , not all of the SO_4^{2-} was consumed.

The concentrations of Au in the various incubation solutions are illustrated in Figure 9.2. Clear differences were observed between the organic-rich samples (1467 and 1468) and the carbonate-rich, organic-poor sample (1470). In general, the dissolution of *in situ* Au (the left-hand graphs in Fig 9.2) was highest for the samples that were irradiated, i.e., biological activity reduces the dissolution of Au. Mechanisms for the suppression of Au dissolution could be decomposition of potential ligands or adsorption of Au by bacteria. This effect was most strongly marked for samples 1467 and 1468, which are higher in the profile, and are more enriched in organic matter. Bubbling with CO_2 also strongly suppressed Au dissolution in these two samples. Dissolution for all treatments was highest for the carbonate-rich sample 1470. This sample also differed in that Au dissolution increased with time even for the non-irradiated samples, and there was little effect from CO_2 bubbling.

Thus, the results for the *in situ* Au dissolution results yield two important conclusions:

- (i) Gold is potentially highly soluble in the samples tested, but tends to be immobilized by biological action. However, the high concentrations of soluble Au (about $10 \mu\text{g/L}$) after one week shaking implies that Au could be mobilized by a single rainfall event;
- (ii) For the normal, CO_2 -bubbled, and irradiated treatments, Au was most extensively dissolved from the most carbonate-rich sample (1470), consistent with the extraction experiments (Section 9.2.2).

When Au was added to the soils (i.e., the graphs on the right-hand side of Figure 9.2), it precipitated from solution, but then, following a lag of about one week for samples 1467 and 1468, began to redissolve. This lag period suggests a biological control, and indeed, irradiation strongly suppressed the dissolution of the added Au. Sample 1470 differed from the other samples in that the precipitation step was slower (up to one week), the subsequent dissolution was nearly linear with time, the CO_2 -bubbled mixtures also showed a

linear, though slower, dissolution, and irradiation had less effect, suggesting that the dissolution was chemically controlled. Thus, the conclusions drawn from the incubation of the Au added treatments are that:

- (i) gold is more soluble when added to the carbonate-rich sample (1470) than when added to samples 1467 and 1468, for periods up to one week;
- (ii) long term (greater than one week) incubation of the organic-rich samples (1467 and 1468) resulted in the formation of solution species with a strong ability to dissolve Au.

Additional work (Report 127R) suggests that this redissolution of Au is a general effect for surface soils containing significant amounts of organic matter, but is not observed for organic-poor soils, nor for other metals, such as Ag. This points to the fundamental importance of biological processes in controlling the mobility of Au in soils.

9.3 SORPTION OF GOLD

9.3.1. Sorption of Au by carbonate-rich soils

The slow sorption of Au from solution by the carbonate-rich sample 1470 (Figure 9.2) suggests that carbonate is relatively poor at precipitating Au. Thus, whereas ferruginous samples from Profile C removed more than 99 % of the Au from solution over 24 hours, samples from the carbonate horizon of Profile B sorbed Au poorly, with up to 16 % of the Au remaining in solution after 24 hours (Report 126R). In addition, other work indicated that the Au thiosulphate was also found to be very poorly sorbed by the carbonate-rich sample 1470 (Report 127R; Section 3.2.2). The carbonate materials thus appear to sorb Au complexes poorly, possibly because at high pH their surfaces tend to be negatively charged and have a poor affinity for Au complexes, which are also generally negatively charged.

9.3.2. Sorption of Au by regolith materials

The sorption of various Au and Ag complexes were tested on differing regolith and soil materials:

- (i) Peat moss: 4 % peat moss with 96 % crushed quartz;
- (ii) 1467: organic rich;
- (iii) 1468: Fe oxide rich;
- (iv) 1470: carbonate rich;
- (v) Std. 7: Fe oxide rich;
- (vi) Mount Keith (MKD): Mn oxide rich;
- (vii) Ora Banda (OB): Mn oxide rich.

Some sample results are shown in Figure 9.3. Each bar represents the proportion of Au or Ag that has remained in solution after two weeks. Important observations, detailed in Report 127R, were that:

- (i) There were widely differing sorption behaviours for the different Au and Ag complexes. Thus, for the chloride solutions (Figure 9.3a), in all mixtures apart from that with the moss, dissolved Ag concentration remained high (90 - 100 %), whereas Au was generally nearly completely precipitated. On the other hand, Au has a higher solubility than Ag in the thiosulphate mixtures (Figure 9.3b).
- (ii) Humate complexes were found to maintain only small concentrations of Au in solution, suggesting a weak interaction between Au and humate. This is in contrast with work on Au humate interactions by other workers (Section 9.4), which has indicated that humate can be very effective at dissolving Au.

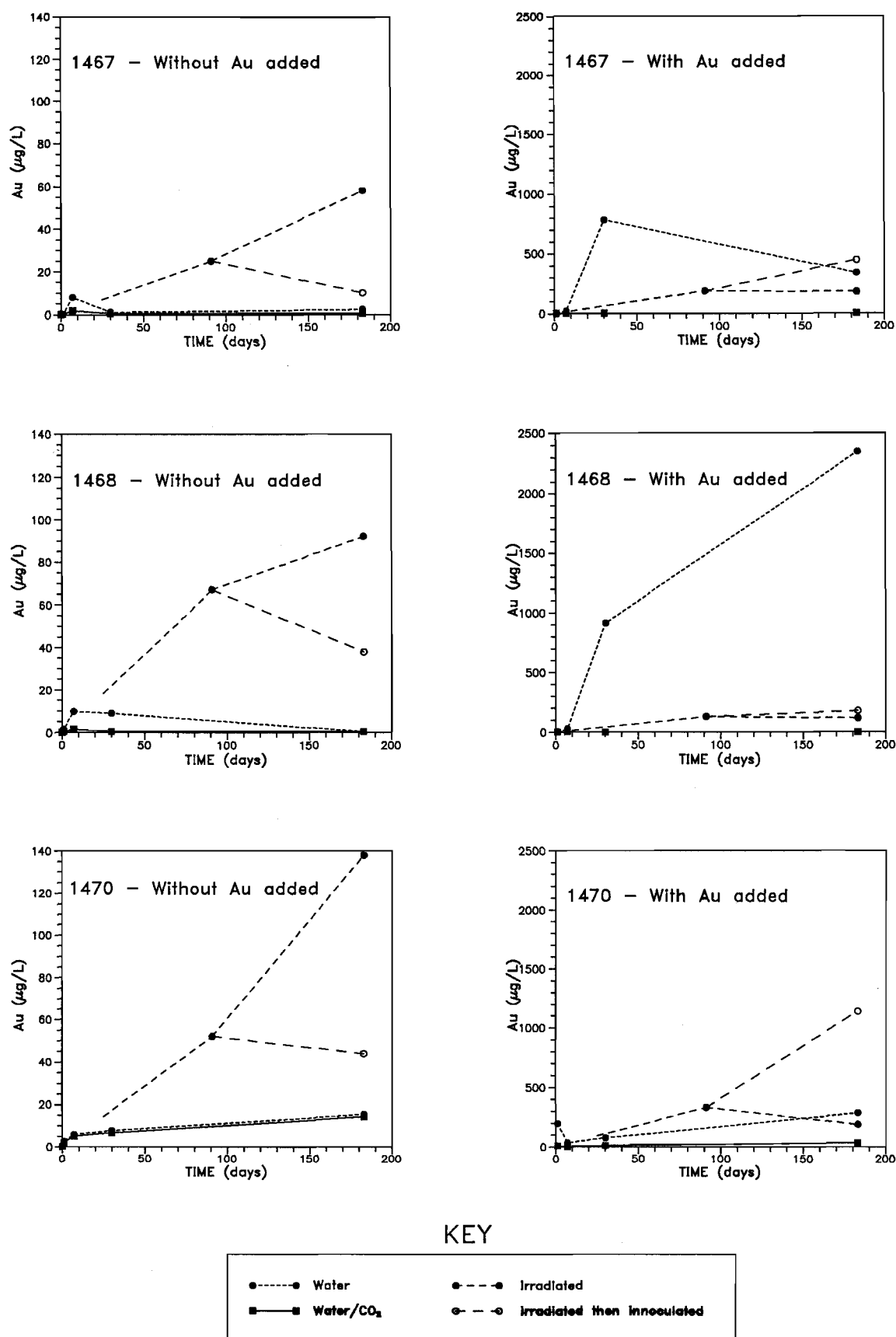


Figure 9.2: Gold concentrations in solutions derived from soil-water incubations. The soil used is given with each graph, and the treatment can be obtained from the key. See Section 9.2.3 for further details.

- (iii) Gold and Ag thiosulphates had a high initial mobility when contacting most of the soils, with the exception of the Mn-rich materials, which sorbed both the Au and Ag (Figure 9.3b). When finally immobilized, Au did not redissolve, implying that it precipitates in an insoluble form.
- (iv) In an acid chloride-rich solution, Au was more highly sorbed on soils than Ag, only being appreciably soluble when in contact with Mn-rich material (Figure 9.3a). Gold iodide had a similar sorption pattern. This supports previous contentions that Ag is more mobile than Au in acid/saline environments, and correlates with hydrogeochemical studies (Section 7.6) that indicate that Mn has a major role in Au mobility under such conditions.
- (v) In the absence of ligands such as iodide or thiosulphate, Au and Ag were readily sorbed but, after three months, significant quantities of Au (but not Ag) redissolved. This is possibly due to soluble species that have a high affinity for Au released by biological activity. Redissolution effects were also observed for Au in the iodide and humate mixtures. Similar mechanisms may be important for Au redistribution in soils.

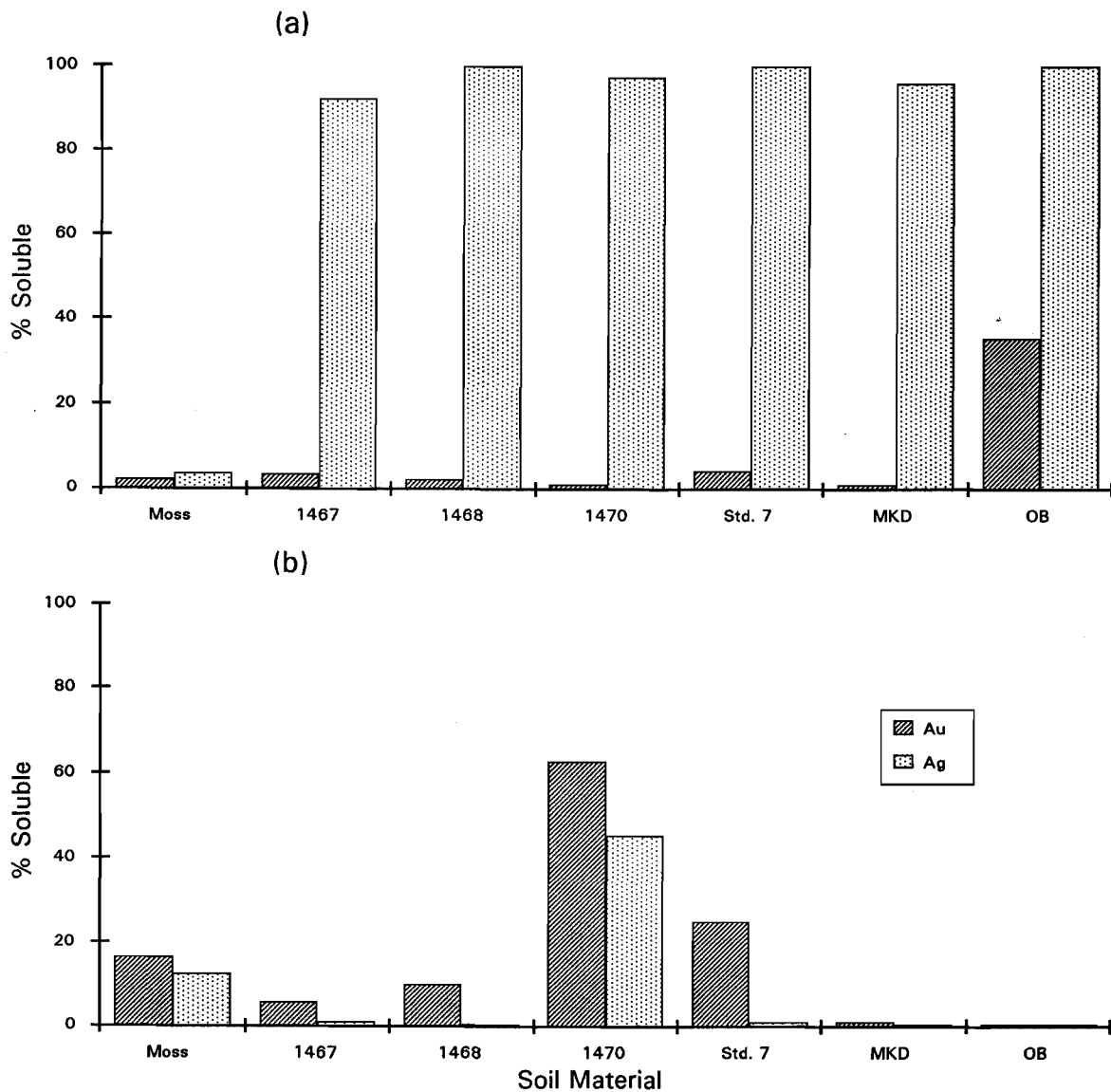


Figure 9.3: Concentration of (a) Au/Ag chloride, and (b) Au/Ag thiosulphate complex, in contact with various soils after two weeks.

9.4. GOLD - HUMIC INTERREACTIONS

9.4.1. Sorption of Au by regolith materials

The chemical interactions of Au with humic matter ('humic matter' denotes amorphous organic substances of molecular weights ranging from several hundreds to tens of thousands) have been studied for several decades. Published results indicate that soluble organic matter either dissolves Au (Freise, 1931; Baker, 1973, 1978; Boyle *et al.*, 1975, Varshal *et al.*, 1984), precipitates Au (Fetzer, 1934, 1946), or forms stabilized colloids with Au (Ong and Swanson, 1969; Fedoseyeva *et al.*, 1986). These contradictory results are probably due to differences in experimental procedures and/or different sources of organic materials. For example, if high concentrations of Au and organic matter are reacted together, then Au may be reduced and precipitated by the organic phase, whereas at low concentrations, organic acids could tend to complex the Au and thus maintain it in solution. Experiments on the reactions of ionic Au with three different sources of soluble humic acid showed that Au interacts with soluble humic matter to form a purple sol (Plate 9.1) that could be investigated by spectrophotometric techniques (Report 128R).

9.4.2. Solubility of gold humate

The factors observed to influence Au solubility were:

- (i) The type of soluble humic matter. Gold solubility is high (> 90 %) for Humate 1 ("Standard" humic acid) and Humate 3 (derived from *Eucalyptus* spp. twigs), and low (9 - 55 % where the initial Au concentration was 1 mg/L or greater) for Humate 2 (derived from *Eucalyptus* spp. leaves). This is indicated in Figure 9.4, which shows the percentage of Au in the < 0.45 μm fraction of various suspensions, after mixing 10 mg/L Au with varying concentrations of two types of humic matter. As can be seen, Au solubility is low when mixed with Humate 2, particularly at higher humic contents (Figure 9.4a), whereas Au solubility is high when in contact with Humate 3, except at lower humate concentrations (Figure 9.4b).

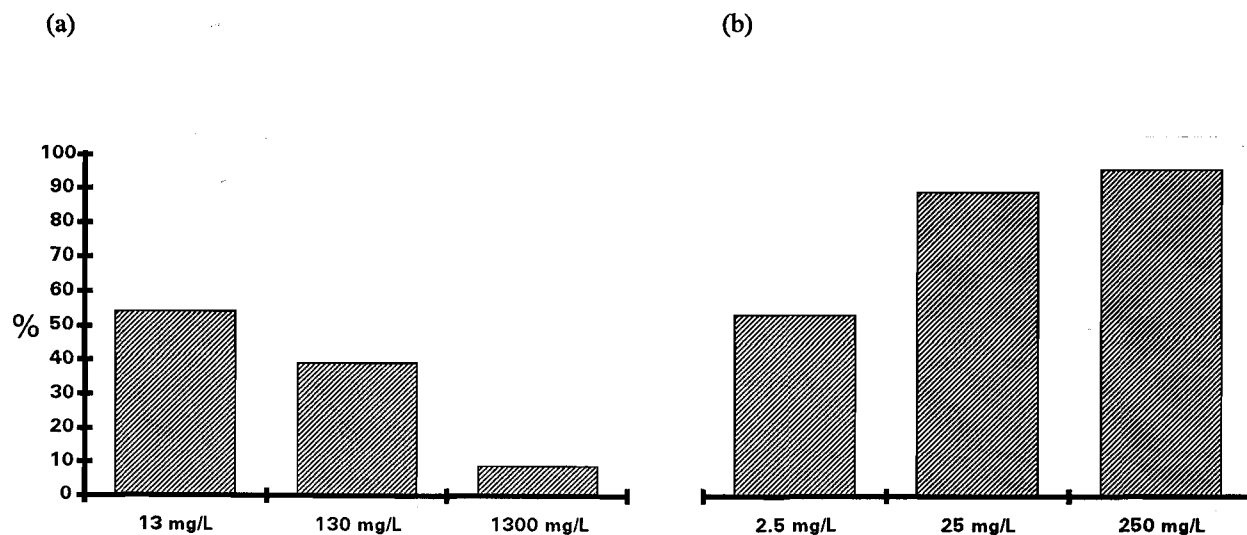


Figure 9.4: Percentage of Au in the < 0.45 μm fraction, where 10 mg/L Au has been equilibrated with varying concentrations of (a) Humate 2 (derived from leaves), and (b) Humate 3 (from twigs).



Plate 9.1

Solutions of gold and Humate 1:-

DG76: 100 mg/L Au, 64 mg/L Humate 1, in the light.

DG77: 100 mg/L Au, 64 mg/L Humate 1, in the dark.

DG78: 10 mg/L Au, 6.4 mg/L Humate 1, in the light.

DG79: 10 mg/L Au, 6.4 mg/L Humate 1, in the dark.

Top: after 2 days. Bottom: after 7 days. See Section 9.4.

- (ii) The concentration of soluble humic matter, in a manner dependent on the humate present. Gold solubility decreases with increasing concentrations of Humate 2 (Figure 9.4a), whereas Au is highly soluble (> 90 %) with Humates 1 and 3, except at low humic concentrations (Figure 9.4b);
- (iii) A solubility limit for Au between 10 and 100 mg/L. Gold will at least partially precipitate from a 100 mg/L Au solution in the presence of soluble humic matter, as seen in tubes DG76 and DG77 in Plate 9.1.
- (iv) The presence of light, which enhances Au solubility. For example, a humic solution containing 10 mg/L Au is purple after 2 days in the light (tube DG78, Plate 9.1) whereas a similar solution left in the dark remains virtually colourless (DG79). After 7 days, the Au colloid has formed even in the dark.

These factors can explain the wide divergence of opinion on the effect of soluble humic phases on Au solubility. Nevertheless, it is not clear why Au humate is stable at Au concentrations of 10 mg/L, but not 100 mg/L, nor why Humate 2 does not stabilize Au in the $<0.45 \mu\text{m}$ fraction as effectively as Humates 1 and 3. A deeper knowledge of both the chemistry of the humate material itself and of the interaction of humate with Au is clearly required in order to understand this potentially important mechanism for Au dissolution and precipitation in natural systems.

9.4.3. Chemistry of the stabilized gold sol

The strong pink/purple colour of the Au sol formed by interaction with humic acids (Plate 9.1) is due to strong light absorbance at about 530 nm. The intensity is proportional to the Au sol concentration. This visible light absorption for the Au humate solutions contrasted strongly with solutions of Au with chloride, iodide, thiosulphate or cyanide, which are all colourless at the same Au concentration.

The results confirmed previous work that the Au sol is formed readily (Fabrikanos *et al.*, 1963; Ong and Swanson, 1969; Fedoseyeva *et al.*, 1986) and that it is stimulated by sunlight. Spectrophotometric data indicated this to occur even when the organic matter was in major excess. The Au sol is effectively decolourized by the addition of ligands with strong (CN^-) or moderate (I^- , $\text{S}_2\text{O}_3^{2-}$, SCN^-) affinities for Au, and even by ligands with weak (Cl^-) affinities for Au, when in high concentration. The tendency for Au to form ionic complexes, rather than a near-neutral sol (also suggested by previous workers; Fedoseyeva *et al.*, 1986; Fabrikanos *et al.*, 1963) implies that the Au sol will only be stable in the *absence* of such ligands. As the unpurified humate preparations (i.e., Humates 2 and 3) readily converted Au to the sol, rather than complexing it, these preparations cannot contain significant concentrations of such Au ligands.

Preliminary work with other metals (Cu, Ag, Pd and Pt) has shown that they do not form sols under the conditions in which the Au sol forms readily.

9.5 DISCUSSION

The experimental work was conducted to gain an understanding of soil processes important to the formation and modification of Au anomalies in soil. Particular emphasis has been on understanding the association of Au with carbonate. The results from the selective extraction tests (Section 9.2.2) and the soil incubations (Section 9.2.3) were surprising in that they implied that Au solubility and extractability was *higher* for Au-rich carbonate horizons, and therefore that these horizons should be *depleted* rather than enriched with Au. This would suggest that the cause of the Au enrichment cannot be primarily chemical.

These experiments also imply that Au is present in a readily soluble form, and that the presence of soluble S- or N-containing molecules may further enhance its solubility. Such organically-derived molecules (i.e., CN^- , thiosulphate or amino acids) have a high affinity for Au (Section 6; Report 4R), and indeed Au should not be considered to behave as a 'noble' metal in soils and other biologically active media. This emphasizes the

critical role of biological activity, which can either dissolve or precipitate Au (Sections 9.2.3 and 9.3.2), depending on the environmental conditions.

Further work on the use of selective extractants (Section 9.2.2), while yielding fundamental information on the chemistry of Au in soils, may also have direct exploration value. The I^- reagent dissolved significant proportions of the soil Au, but in a manner that is highly dependent on the form of the Au. Work to date has investigated variations in the relative proportions of Au extracted down a profile. There may also be lateral trends in the extractability of Au, which may give information on the age of the soil anomaly and possibly its proximity to mineralization.

The sorption experiments (Section 9.3.2) indicate that Au sorption is dependent not only on the aqueous conditions and the regolith mineralogy, but also on the form in which the Au was initially dissolved. Thus, Au dissolved due to acid chloride oxidation will have a low solubility except where Mn is present at high concentrations, whereas Au dissolved by neutral or alkaline sulphide weathering (i.e., Au thiosulphate; Section 6.2.2) will have a moderate solubility, but is strongly immobilized by the presence of Mn oxides. The soluble form of the Au not only effects the degree of sorption, but also the form in which the Au precipitates: Au precipitated from the thiosulphate complex is strongly resistant to redissolution, whereas Au complexed by iodide, humate or water precipitated in a form that readily redissolved over several months, presumably due to production of ligands by biological activity.

The interaction of Au with humic matter (Section 9.4) has indicated complex controls on Au solubility. In the absence of ionic ligands, Au reacts with humate to form either precipitated Au or a Au sol. Gold is known to be incorporated into plants, both in the southern Yilgarn study areas (See Section 11 and Reports 24R and 129R) and elsewhere (Smith and Keele, 1984; Erdman and Olson, 1985). When leaves and woody matter containing Au fall to the ground and decompose to humus, the Au sol may be formed in this upper soil layer. The stability of the sol may be highly dependent on presence of other ligands, such as amino acids, Br^- or I^- , which are released with organic matter decomposition, and thus could decompose the Au sol into other soluble or insoluble forms lower in the soil profile. Thus, the Au-humate interaction may have some role in Au mobility and on the formation of Au soil anomalies.

The general conclusions derived from the available experimental data are that Au may be strongly mobilized by biologically-controlled species, can also be immobilized by biological processes, and generally appears to be most chemically mobile within carbonate-rich zones. Why then is Au most strongly correlated with carbonate, as found widely in the southern Yilgarn block (Section 8)? One possible hypothesis is that Au distribution is at least partially controlled by evaporative as well as evapotranspirative processes. Thus, Au, as discussed above, can be highly mobile in upper soil horizons, associated with biologically generated ligands. Such Au-organic complexes may be very stable against adsorption or precipitation and will percolate down the soil profile. However, once these complexes reach the carbonate horizon, they will be immobilized by the loss (e.g., by evaporation) of water, which also causes precipitation of additional carbonate, halite and other salts. Thus, the primary controls on Au distribution in these soils are postulated to be biological and physical, rather than purely chemical, as first expected.

Clearly, this hypothesis has implications for the type of soil anomalies expected in various environments. The presence of carbonate indicates an evaporative horizon and the probable immobilization of Au, whereas the absence of carbonate indicates that Au dissolved by biological activity may be leaching from the upper soil profile due to the lack of any hydrological trap. Similar work is required for areas north of the Menzies line, in soils which are not actively precipitating carbonate, to see whether their characteristics are compatible with this theory for Au redistribution in soils, and to investigate the implications for Au exploration using soils in other weathering environments.

10.0 LAG AND SOIL GEOCHEMISTRY - BEASLEY CREEK

10.1 GEOMORPHOLOGY

Mining at Beasley Creek has provided an opportunity for an integrated study of the surficial materials and the saprolite at Beasley Creek involving all three modules of the CSIRO/AMIRA Gold Project. Surficial materials were mapped and soil and lag samples were collected along two traverses over the mine site and into the background. This study has been covered by Reports 26R (geomorphology), 27R (lag) and 105R (soil). The landscape around the Beasley Creek Gold Mine has a first impression of simplicity but is actually quite complex (Figure 10.1). Surface geochemical media are elements of this landscape, so it is essential to understand them in order to select the best materials and interpret the results.

The Beasley Creek Gold mine is on a small rise 3.5 m above the surrounding wash plains, which together form a low, tabular divide between broad drainage floors to the north and south. The rise is asymmetric, with a very gentle western slope, marked by calcrete and sparse, small, outcrops of saprolite. The crest has sporadic outcrops of ironstone and the steeper eastern slope is protected by lateritic duricrust. The regolith at Beasley Creek has been partly stripped. A ferruginous, lateritic duricrust closely follows the upper surface of an ore-bearing black shale unit and it seems likely that Fe in the shale, probably originally as sulphides, was the source of Fe in the lateritic duricrust. Ironstones overlie both the ore-bearing black shale and metadolerites.

The whole area, including the rise, is mantled by red, friable clay soil and strewn with multi-component lag which was derived by selective removal of the fine fractions of the soil by sheetwash and deflation. The soils on the low-lying areas are deeper (0.3-0.45 m) than on the rise, are relatively acid and are underlain by hardpan; they become alkaline and thin (0.1-0.2 m) on the rise, where they are underlain by saprolite and calcrete. The distribution of a duricrust-related khaki lag closely follows the hanging wall of the black shale orebody. A coarse, black, ferruginous lag has a wider distribution, but seems associated with the subcrop of the host black shale and is concentrated within 200 m of its source. An ironstone lag is dispersed around small ironstone outcrops and also appears to be spread no more than 200 m from source. Finer, brown, ferruginous lags have a wider distribution and their finest fractions have been partly separated by down slope colluvial sedimentation. Quartz lag is dispersed around small quartz veins, unrelated to ore.

The lags and soils were analysed to assess their value as sample media. The fine (0.2-4.0 mm) and coarse (10-50 mm) fractions of the black ferruginous lag were studied physically, petrographically, mineralogically and geochemically. The fine lag was split into magnetic and non-magnetic components. The soil was separated into several size fractions for mineralogical and geochemical analyses.

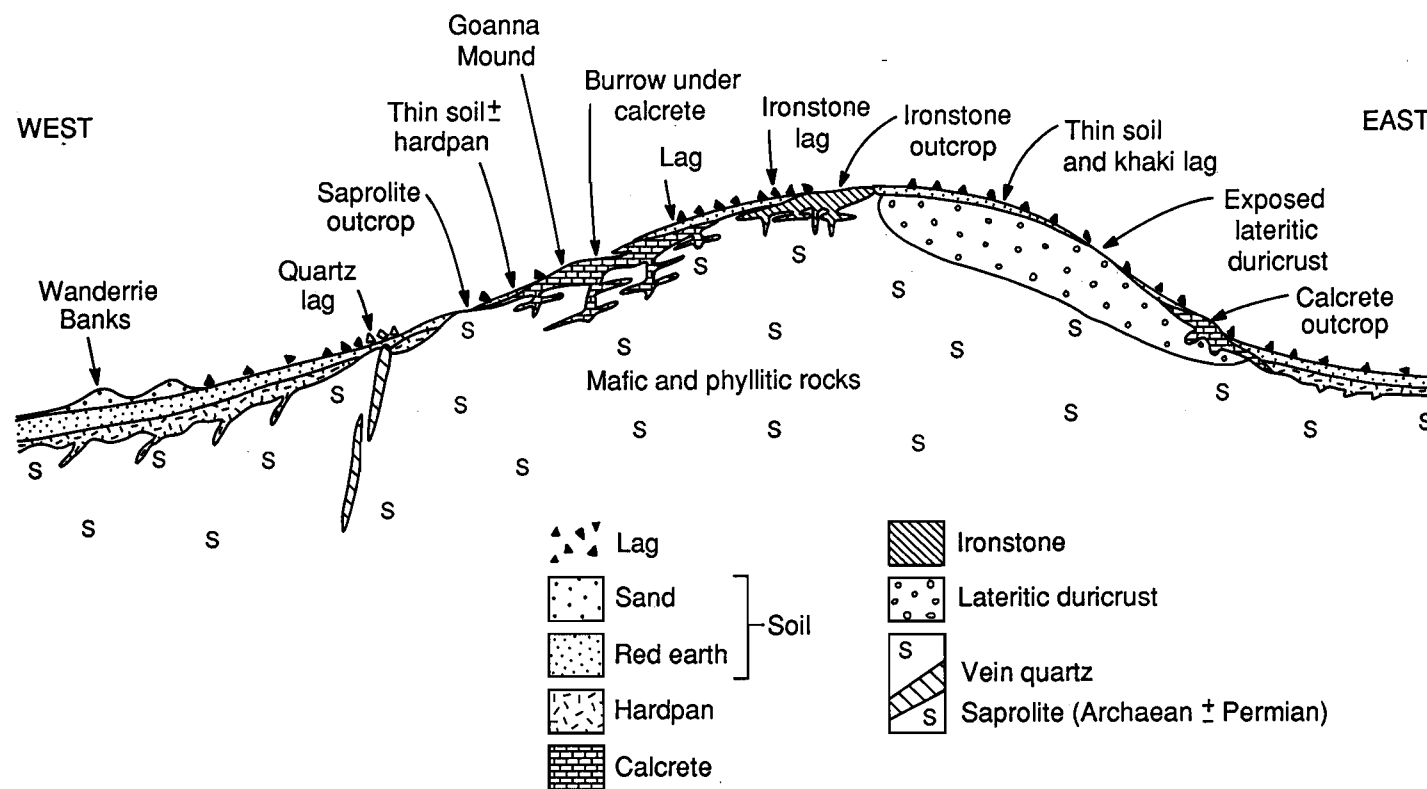
10.2 LAG

10.2.1 Mineralogy and petrography

The black ferruginous lag consists mainly of goethite and hematite with minor kaolinite, illite, quartz and interstratified clay. The hematite and goethite contents appear to be complementary. Background lag samples are richer in kaolinite, quartz and hematite and poorer in goethite than those nearer ore.

The lag contains ferruginized lithorelics with relict and pseudomorphed minerals and fabrics inherited from the underlying primary lithology, the saprolite and the plasmic horizon. The phyllitic host rock is indicated by relics of slightly K-deficient mica and kaolinite. The mafic and ultramafic rocks are shown by "fingerprint" fabrics after saprolitic clays. Goethite pseudomorphs kaolinitic accordion structures which, originally, were either saprolitic or plasmic fabrics rather than fabrics of the fresh rock. The Permian glacial sediments are reflected by polymictic breccia fabrics.

Figure 10.1 Sketch cross section of the hill at Beasley Creek showing relationships between major surficial materials (not to scale).



The lithorelics are surrounded by several phases of secondary goethite and hematite, which have obliterated much of the original fabric. Hematite appears to be a dehydration product of goethite. Later history is shown by skins and complete nodules of ferruginous clay that have undergone several cycles of solution, clay precipitation and permeation by Fe-bearing solutions. The fine lag contains additional minor components of calcrete, quartz and fragments of a geochemically very important cellular ironstone or gossan.

Fabric information from the coarse lag may be used to determine the underlying lithologies of lag-covered areas, without the need for drilling. Although the fine lag has similar fabrics, it is finer, more fragmentary and more widely dispersed, so that elucidation of the original rock type is more difficult.

10.2.2 Geochemistry

Lags derived from the orebody are anomalous in Au, As, Ba, Co, Cu, Fe, Mn, Mo (weak), Pb (possible), Sb, W and Zn. The cellular ironstone appears to be responsible for much of the anomalous As, Au, Co, Cu, Mn, Sb, Se and Zn. Gold is the best indicator of mineralization and shows strong anomalies (1000 ppb over a 10 ppb background) which are 600 - 900 m wide. Other elements show narrower dispersions. Superimposed on these broad Au anomalies are narrow, subsidiary peaks (> 10,000 ppb), specifically in the coarse lag, which accurately locate the ore. The wide Au halo reflects its distribution in the underlying rocks, prior to mechanical surface dispersion of the lag. The very distinctive Mn and Ba anomalies are thought to be related to the ore host rock rather than to the ore itself.

Both the coarse and the fine lags are effective geochemical media because key indicator elements are readily adsorbed by goethite, their major component. Intense Au spikes in the coarse lag locate the orebody more precisely than the more dispersed fine lag. The fine lag gave better results for Sb, W and Zn. The non-magnetic component of the fine lag was geochemically superior to the magnetic component as it contains the gossanous fragments. As the non-magnetic component makes up about 75% of the total lag, only a slightly improved performance could be gained by analysing it separately. However, considerable improvement would be possible if the minor cellular ironstone could be treated separately, but use of such a specific material would then be entirely dependent on sufficient gossan fragments reaching the surface. Furthermore, the adsorbed metals on other goethitic materials should not be ignored.

10.2.3 Dispersion and origin

The fine lag is readily transported by surface water, even down a very slight gradient, but the coarse lag requires either a significant gradient or introduction into a drainage to move any distance. In general, the finest fractions of the fine lag show the greatest dispersion and the coarser fractions show progressively lesser dispersion. The more dispersed fine lag is better for defining the general area of mineralization in a first-pass survey; the coarse lag should be used for follow-up. The distribution of the khaki lag and the ironstone lag are not sufficiently universal for them to be used effectively as geochemical sampling media.

The potential of a lag as a geochemical sampling medium depends upon its geomorphic setting and on the underlying geology. Lag derived from weathered Permian glacial sediments would be of little or no use, nor would that derived from a thick blanket of recent transported overburden. Lag derived from underlying duricrust, and from the saprolite of partly eroded areas, has the best potential. It is therefore necessary to map the geomorphology and, as far as possible, the underlying geology in order to subdivide the geochemical data prior to statistical treatment.

10.3 SOIL

10.3.1 Soil fractionation and mineralogy

The soil consists of three contrasting fractions:

- (i) A coarse, saprolite-derived fraction ($>710\ \mu\text{m}$; petrographically indistinguishable from the lag) that consists of dense, goethitic granules (some magnetic), slightly less-dense, ferruginous, clay pebbles and granules, a few quartz grains, fragments of calcrete, hardpan and rare cellular gossan. The proportion of gossan fragments is significantly greater close to the orebody. The goethitic granules are analogous to the lag and consist of mica relics, goethite pseudomorphs after kaolinitic lithorelics and vermicular accordion structures, set in a variety of secondary goethite phases. The clay-rich granules consist largely of hematite- or goethite-stained kaolinite and some include goethite-rich lithorelics.
- (ii) An intermediate fraction ($75\text{--}710\ \mu\text{m}$) that consists largely of hematite-coated, wind-blown quartz and minor grains of feldspar, which act as geochemical diluents. This fraction was not studied further.
- (iii) A fine fraction ($<75\ \mu\text{m}$) that consists of quartz grains and smaller kaolinite and Fe oxide particles partly locally derived by breakdown of clay pisoliths and granules, and partly wind-blown. This fraction was separated further by clay sedimentation, using pH control, into relatively quartz-rich ($<75\ \mu\text{m}$) and the clay- and Fe oxide-rich ($<4\ \mu\text{m}$) fractions. The $<4\ \mu\text{m}$ fraction shows maximum abundances in both kaolinite and sericite over the ore, probably related to the phyllitic host rock.

The geochemical expression of mineralization in the different size fractions of the lag and soil are compared in Table 10.1.

10.3.2 Geochemistry

The geochemical characteristics of the $710\text{--}4000\ \mu\text{m}$ fraction and the fine lag are identical. Gold is distinctively anomalous, giving a very broad peak of >20 ppb but locally reaching $200\text{--}300$ ppb. The $710\text{--}4000\ \mu\text{m}$ fraction is the most effective medium, with the highest values and the greatest anomaly to background contrast. The orebody is also depicted by anomalies in As, Cd, Cu, Sb, Se, W and Zn and the host rock by Ba and Mn. A maximum in S over the ore is related to a subcropping gypsiferous horizon. Although As is concentrated in the $710\text{--}4000\ \mu\text{m}$ fraction, the anomaly to background contrast is better in the fine fractions. There is a small Pb anomaly (50 ppm in a background of 30 ppm) in the coarse lag but no corresponding anomaly in the fine lag or the soil. Sulphur is anomalous in all fractions. Increased geochemical noise in Co, Ni and V over the rise at Beasley Creek reflects the saprolites of Archaean rocks buried under a shallow, residual soil. This may be contrasted with the lesser geochemical noise in these elements, over weathered Permian rocks, possibly buried under a slightly deeper, colluvial soil. There is a decrease in the Si abundance over the ore host rock, whereas Fe in the lateritic duricrust shows a complementary increase.

10.4 IMPLICATIONS FOR EXPLORATION

Gold anomalies, and particularly their contrast, are greatly improved by the use of the coarse, ferruginous $710\text{--}4000\ \mu\text{m}$ fraction, in preference to the complete soil. Apart from Au, anomalies in As, Cd, Cu, W and Zn comprise the useful multi-element signature of Beasley Creek. The effectiveness of the various sampling media are summarized in Table 10.1 in terms of peak to background ratio, anomaly width and clarity of the anomaly.

Table 10.1

Comparison of anomaly widths and peak to background ratios in Beasley Creek.

COMPARISON OF ANOMALY WIDTHS
AND PEAK TO BACKGROUND RATIOS

	COARSE LAG		All		FINE LAG		Non-magnetic		Complete Soil		SOIL		<75 µm		<4 µm		Possible Source
	Peak P/B	Width (m)			Peak P/B	Width (m)					Peak P/B	Width (m)	Peak P/B	Width (m)	Peak P/B	Width (m)	
Au	100/5	900/100	100	900	5	600	7	700	6.5	900/200	30	300	5	900/100	8.3	900/200	Supergene
As	3	100	2	100	?		2.5	100	3	100	3	200	3	100	3	100	Ore
Sb			1.5	300	?		1.5	100	1.5	200	1.5	200	-		-		Ore
Se	2	100	1.5	100	-		2	100	2	200	1.5	300	-		-		Ore
Cu	2	100	2	200	-		1.5	200	2	200	2	200	-		2	200	Ore
Pb	2	100							-		-		-		-		Ore
Cd	-		-		-		-		3	300	6	200	?		4	100	Ore
Zn	?		1.5	100	-		1.5	100	1.5	200	2	200	1.5	200	1.3	200	Ore
Co	2	100	1.5	100			1.5	100	-		?		-		-		?
W	?		3	100	?		2	300	?	100	4	200	?		3	200	Ore
S									4	300	3	300	6		5	200	?
Ba	5	300	7	300	8	300	6	300	2.5	200	15	300	?		?		Host Rock
Mn	15	200	6	200	?		7	200	3.5	300	3.5	200	2.5	300	5	300	Host Rock

The soil has been diluted by wind-blown sand and, in its complete form, is less effective than its fractions. The quartz-rich 75-710 μm fraction should be removed, by sieving, prior to analysis. The most effective media are the coarse, ferruginous 710-4000 μm soil fraction and its analogous fine lag, followed by the <4 μm soil clays. The <75 μm silty soil fraction also contains a significant wind-blown, sandy component and is the least effective size fraction together with the clearly wind-blown 75-710 μm fraction. Preferential use of the coarse and fine fractions has similarly been recommended by Barbier (1987), Salpeteur (1985) and Salpeteur and Sabir (1989) in Saudi Arabia, where aeolian dilution is more severe. Mazzucchelli (1980) was able to achieve a similar improvement by partial extraction (acetic acid) of the fine (<175 μm) soil fraction (presumably of Fe oxides), in aeolian-diluted soils in the Warburton area of Western Australia.

Fine lag is an excellent sampling medium. Only a very marginal improvement may be gained by using the non-magnetic portion of the fine lag but it is doubtful if the improvement would be worth the extra cost of separation. The coarse lag fraction (10-50 mm) will find use in follow-up work and for assisting geological mapping. The enhanced dispersion of Au in the soil clay fraction, together with proven responses in As, Cd and Cu, suggests that it could be used for drainage surveys in areas of low relief. Its separation from the soil does not present any great technical difficulties.

Size fractionation and microscopic examination of the components of both soil and lag during orientation surveys and during the exploration process will contribute to an understanding of the history of these materials. Information gleaned from this will ensure that the correct media are collected, detect gossan fragments and help with interpretation of results.

11.0 BIOGEOCHEMICAL EXPLORATION FOR GOLD

11.1 INTRODUCTION

The major perceived advantage that biogeochemistry has over soil sampling is that plants, particularly trees, have the potential to sample material from greater depths and wider areas. The Au composition of vegetation reflects, to a great extent, (a) the availability of Au in the vicinity of the root system and (b) the ability of the plant to absorb, transport and accumulate Au. Products derived from vegetation e.g., mull (decaying plant material) may contain concentrations of elements in excess of the original plant material due to preferential leaching of more mobile constituents.

Biogeochemistry has not been widely used as an exploration technique. It has not been applied extensively in Western Australia (or elsewhere) for two main reasons. Firstly, soil sampling and other surficial techniques have been reasonably effective in delineating concealed deposits. Although biogeochemistry has been used to supplement data from soil geochemical surveys, no economic deposit of Au, or any other commodity in Australia, has been found specifically by biogeochemistry. Secondly, interpretation of the data requires a consistent and regionally typical sample. This is feasible in Canada, for example, where a few plant species are widely distributed, but in Australia, species can vary considerably even within a few tens of metres and are difficult to recognize.

Biogeochemical sampling must ensure a consistent plant organ is sampled e.g., leaves, bark, roots or branches, and take into account the age and health of the plant, genetic variation and the time of year sampled. Furthermore, comparisons between the geochemistry of soils and vegetation should be considered with care, since the soil horizon sampled may not necessarily reflect the zone utilized by the plant species for nutrients and water. The location of the root system of plants in semi-arid areas predominantly reflects the availability of water, i.e., rainfall and soil structure. Many plant species have adapted to dry conditions (e.g., saltbush) by having some of their roots very close to the surface so they can readily absorb water from minor rainfall events before it evaporates. Other plants, e.g., *Eremophila* spp., have root systems that occur extensively within the top metre (rather than at the surface). *Eucalyptus* spp. can have, in addition to the near-surface root system, a long tap root (sometimes tens of metres in length) capable of absorbing nutrients and water from very deep in the profile. Nutrients and water absorbed by *Eucalyptus* spp., therefore, might represent a composite of that obtained by roots from two or more depths within the profile.

The potential of biogeochemistry has been tested at Mt. Hope (Report 24R) and Panglo (Report 129R). All concentrations are calculated relative to ashed weight of oven-dried (105°C) material unless otherwise stated. Ashing concentrates the non-volatile elements in the sample by a factor of about 20-fold.

11.2 MT. HOPE

The survey undertaken at Mt. Hope was restricted to a selection of different plant species located near a series of soil sampling pits (Report 24R). The results indicated that the minimum and maximum Au concentration range for plants is approximately coincident with the minimum and maximum concentrations for soils. Concentrations below detection (<0.040 ppm) were recorded for several plant species in background areas, to a maximum of 0.312 ppm for *Alocasuarina* spp. close to mineralization. The Au content of mull varies from below detection limit (<0.010 ppm) at background to 0.585 ppm (above mineralization) and was generally higher than concentrations found in the vegetation. This suggests that some Au is at least partially retained whilst the vegetation undergoes decomposition and leaching of other components. The concentration of Au found in mull samples after ashing the samples generally has a similar concentration to that found within the dried soil. All of the major plant genera sampled (*Eucalyptus* spp., *Melaleuca* spp. and *Daviesia* spp.) contain some Au, but no particular genus is outstanding as a Au accumulator.

A detailed study of Au distribution was made within a single tree (*Eucalyptus flocktoniae*) growing in the vicinity of mineralization. The results showed that the leaves have the highest Au contents, although quantitatively most Au is contained within the trunk, since this has the greatest mass (Table 11.1).

Table 11.1. Gold content in parts of *Eucalyptus flocktoniae*. Leaves and branches were subdivided into two batches (1 and 2) to test for variation.

Sample Type	Au content ppb (dry weight)	Total mass Kg	Total Au μ g
Leaves (1)	3.3	0.323	1.07
Leaves (2)	2.7	0.249	0.67
Branches (1)(<5 mm dia)	1.8	0.190	0.34
Branches (2)(<5 mm dia)	<0.5	0.108	<0.05
Branches (>5 mm dia)	2.2	0.595	1.31
Bark	1.1	0.061	0.07
Trunk	2.0	4.175	8.35
Root	1.6	0.864	1.38
Totals		6.565	13.19

11.3 PANGLO

Plants were sampled on two traverses (3700N and 4200N) at Panglo, across the southern edge and centre of mineralization, respectively (Figure 7.1). The distributions of different plant species are determined by soil type, geomorphology and lithology. These vary considerably along the traverses, so that different plant species were found growing on each. Problems involving sample representativeness were partly overcome by sampling several species and grouping them according to their genera, and by sampling vegetation with similar trunk diameter and/or height.

The results indicated that Au concentrations in vegetation on line 4200N across the centre of mineralization (see Figure 8.3) are generally close to background and show at best a poor association with either Au in soils, lithology or economic mineralization. The soils are characterized by a sandy top-soil and a saline, clay-rich sub-soil. The vegetation is dominated by salt-tolerant, shallow rooted shrubs with few trees. Higher Au contents were found in *Eremophila* spp. (mean = 0.014 ppm, n = 12, maximum = 0.024 ppm) and *Melaleuca* spp. (0.132 ppm), compared with *Atriplex* spp. (mean = 0.004 ppm, n = 15, maximum = 0.018 ppm). The highest Au content (0.185 ppm) was recorded for *Dodonaea* spp. (a small shrub) but, because its distribution was limited, only one specimen of this plant was sampled and it is not known whether this Au content is anomalous in relation to other *Dodonaea* spp.

The distribution of Au shown by vegetation sampling on line 3700N across the southern edge of mineralization is broadly similar to that found in the soil, though contrasts tend to be higher in the gravel-rich soils. The soils and dominant vegetation type change across the traverse from gravels and trees (*Eucalyptus* spp.) associated with the palaeochannel (see Figure 8.5), to thin soils composed of material derived from sub-cropping saprolite, to clay-rich colluvial material in the drainage channel with small, salt-tolerant shrubs, and to clay loams supporting trees (*Eucalyptus* spp.) on the other side of the drainage. Gold contents are significantly higher in *Eremophila* spp. (mean = 0.013 ppm, n = 21, maximum = 0.059 ppm) than *Eucalyptus* spp. (mean = 0.008 ppm, n = 17, maximum = 0.042 ppm). *Eucalyptus* spp. in areas to the east of the traverse contain more Au (mean = 0.020 ppm) than *Eucalyptus* spp. found over mineralization to the

west (mean = 0.002 ppm) and may be of significance since they are also nearly double the regional background (0.012 ppm). Furthermore, the background data suggest that *Eucalyptus* spp. are not as effective as *Eremophila* spp. in accumulating Au. The Au content of *Eremophila* spp. over mineralization on 3700N are generally greater than those over mineralization on 4200N.

11.4 THE ROLE OF PLANTS IN CALCIUM CYCLING

Calcium is an important vegetation macro-nutrient, primarily required for mechanical strength, and was found in significant concentrations within some species e.g., in excess of 30%, which is greater than that found in most soils. In the four major plant genera examined, Ca concentrations are generally highest in *Eucalyptus* spp., followed by, in decreasing order, *Melaleuca* spp., *Eremophila* spp. and *Atriplex* spp. There is some evidence that soil Ca content may be related to vegetation Ca content. For example, at Panglo, Ca enrichment in *Eremophila* spp. is greater on 3700N than on 4200N, which reflects the relative abundances of pedogenic carbonate in the soil, and soil Ca contents are generally greater beneath *Eucalyptus* spp., already noted for high Ca contents. The significance of the cycling of calcium in the soil has been discussed in relation to the associations between Au and pedogenic carbonate (Section 8). If vegetation, and trees in particular, are shown to be a major contributor to the soil Ca cycle, then the strength and size of some soil Au anomalies may be closely related to vegetation cover.

11.5 CONCLUSION

Vegetation Au contents are generally less at Panglo than at Mt. Hope and Norseman (Smith and Keele, 1984), particularly over mineralization. This probably reflects the depth to mineralization, which at Panglo is at about 40 m and at Mt. Hope at only a few metres. *Melaleuca pauperiflora* was sampled at Norseman and Au concentrations were found to correlate with the upward projection of the shear zones containing Au mineralization, rather than with the soil Au anomaly, which occurs directly above mineralization. Anomalous Au concentrations of 0.100 - 0.150 ppm with a peak of 0.230 ppm against a background of less than 0.060 ppm were found in *M. pauperiflora*. At both Panglo and Mt. Hope, shrub species (*Eremophila* spp. and *Melaleuca* spp.) have higher Au concentrations than the trees (*Eucalyptus* spp.) over mineralization. The reason for this is unclear: one explanation is that the shrubs have a higher capacity to either absorb or retain Au, as they have with Cu.

Despite the presence of Au in vegetation and the role that vegetation may have in contributing to soil Au anomalies, biogeochemistry cannot be used alone as an exploration tool as it does not correctly define the tenor and location of underlying mineralization in all cases. Though there is some evidence on line 3700N at Panglo for a weak relationship between Au in vegetation and Au in soils, on line 4200N, there is little indication that the Au content of vegetation reflects either Au in soils or mineralization at depth. At Mt. Hope, there is a general relationship between Au in soil and that found in vegetation. Mull sampling may be a better geochemical medium, but sample preparation and, in particular, the tedious removal of inorganic contaminants, may preclude the technique for general use. Mull contributes ultimately to the composition of the soil.

12. FUTURE RESEARCH: PROJECT 241A

It is evident that there is still considerable scope for further research in most of the topics identified for investigation in Project P241. Following discussion with sponsor companies, the most important of these have been selected for study during a two year extension of the Project (AMIRA Project 241A). The proposed research topics include:

1. *Atlas of Rock Weathering*

During previous research and the course of Project P241, material and data have been accumulating, suitable for the depiction of actual profiles with petrographic data at "hand lens" and microscopic scale, mineralogy, geochemistry and other information. It is proposed to assemble these data in the form of an Atlas of Rock Weathering, depicting a wide range of lithologies. Additional profiles from Reedy, Telegraph pit (Lancefield), Bottle Creek, Cork Tree Well and Mt. Percy will be included. Some other data are incomplete and some important lithologies are not represented, so that further sampling and analysis will be carried out where appropriate. The atlas will be produced in loose-leaf format, each lithology issued as it is completed.

2. *Gold mineralization and profile development*

- a. Interpretation of the dispersion studies at Lights of Israel (Davyhurst), Bottle Creek and Telegraph (Lancefield) gold mines. The samples were collected during Project P241, but time constraints prevented further study.
- b. Analysis and interpretation of the "background" bedrock and regolith study at Mt. Percy. This site is along strike from the mineralization being studied in the Mystery Zone and will therefore provide an important control on the interpretation of those data.
- c. Geochemistry, mineralogy and micromorphology of the development of mottles and pisoliths in clay-rich horizons, (in collaboration with Project 240A).
- d. A study of geochemical dispersion in the deep regolith in a humid savanna environment in Northern Australia. This is expected to represent a modern analogue of the environments under which the deep weathering of the Yilgarn Block occurred, prior to the post-Miocene change to aridity. The study will also provide information of value to exploration in savanna regions themselves.

3. *Gold distribution in the near-surface*

- a. Investigation of the role of pedogenic carbonates in concentrating gold where mineralization is concealed by barren transported overburden or a leached zone of gold depletion. The research will investigate the relationship between anomaly size and tenor, thickness of barren overburden and significance of mineralization.
- b. Investigation of the fate of gold in areas in the northern half of the Yilgarn Block (north of the "Menzies Line"), which are commonly characterized by the presence of red-brown hardpan. The mechanism by which gold and calcium are mobilized by vegetation is presumably still active, but there is little or no pedogenic carbonate and gold does not appear to be concentrated in the soil. A detailed investigation of the vegetation, soil, hardpan and upper regolith over mineralization in such an area may indicate a preferred site of gold enrichment.
- c. Interpretation of the soil survey at Lights of Israel mine.
- d. Collaboration with Project P243 (Remote Sensing): interpretation of soils and landforms over the Mt. Hope and Beasley Creek areas, based on surveys completed under P241.

4. *Hydrogeochemistry and low temperature chemistry of gold*
 - a. Hydrogeochemistry of palaeodrainages. A considerable amount of gold has been eroded and leached from the Yilgarn Block during its long history of sub-aerial weathering. The fate of this gold is largely unknown, but clearly it must have entered the extensive, now mostly choked, drainage systems. Apart from the deep leads in the Kalgoorlie region, few of these have been investigated in detail, although it is known that secondary gold is present in some, precipitated at redox fronts distal from the source. It is proposed to study the hydrogeochemistry of some drainages close to known mineralization to determine the preferred sites for precipitation that might thus constitute an exploration target.
 - b. Gold chemistry. Confirmation of results obtained to date and further investigation of the high solubility of gold in some soil materials, the potential of ligands such as iodide for some selective gold extractions and the role of organic matter in gold mobility. The electrochemistry of gold and the relationship between the morphology of secondary gold and solution chemistry may also be studied.

The final selection of some of these topics and the emphasis placed on them are subject to the availability of suitable sites and materials, and to the resources of the Project.

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APPENDIX 1. REPORTS ISSUED BY PROJECT P241

- MG58R Morphology and geochemistry of gold in a laterite profile, Reedy Mine, Western Australia.
P. Freyssinet and C.R.M. Butt. April, 1988. 18pp
- MG59R Morphology and geochemistry of gold in a laterite profile, Bardoc Mine, Western Australia.
P. Freyssinet and C.R.M. Butt. April, 1988. 28pp
- MG60R Morphology and geochemistry of gold in a laterite profile, Beasley Creek, Laverton, Western Australia.
P. Freyssinet and C.R.M. Butt. April, 1988. 14 pp
- MG67R A mineralogical, geochemical and petrographic study of the rocks of drillhole BCD1 from the Beasley Creek gold Mine - Laverton, W.A.
I.D.M. Robertson and S.F. Gall. June, 1988. 47pp (Project P241 report also issued to Project P240).
- 4R The aqueous chemistry of gold in the weathering environment.
D.J. Gray. December, 1988. 65pp (Joint report with Project 240)
- 23R Occurrence of gold in hardpan, Youanmi Mine.
A.Z. Gedeon and C.R.M. Butt. May, 1989. 10pp
- 24R Study of the distribution of gold in soils at Mt. Hope, Western Australia.
M.J. Lintern. May, 1989. 36pp
- 26R The pre-mining geomorphology and surface geology of the Beasley Creek gold mine - Laverton, W.A.
I.D.M. Robertson and H.M. Churchward. July, 1989. 39pp (Joint report with Project 240).
- 27R Geochemistry, petrography and mineralogy of ferruginous lag overlying the Beasley Creek Gold Mine - Laverton, W.A. Volumes I and II.
I.D.M. Robertson. November 1989. 181pp (Project P240, issued also to Project 241).
- 32R Mineralogy and Geochemistry of weathered shale profiles at the Panglo Gold Deposit, Eastern Goldfields, W.A.
K.M. Scott February, 1989. 21pp
- 33R Mineralogy and geochemistry of mineralized and barren weathered profiles, Parkinson Pit, Mt. Magnet, WA.
K.M. Scott. February, 1989. 24pp
- 36R Mineralogical and geochemical studies of gossan and wall rocks, Bottle Creek, Western Australia.
G.F. Taylor. July, 1989. 35pp
- 41R Radioelements in weathered shales and mafic volcanics, Panglo gold deposit, Eastern Goldfields, W.A.
K.M. Scott and B.L. Dickson. April, 1989. 31pp (Joint report with Project P263)
- 42R Mineralogy and geochemistry of weathered mafic/ultramafic volcanics from section 4200N at Panglo, Eastern Goldfields, W.A.
K.M. Scott. April 1989. 22pp
- 43R Mineralogy and geochemistry of some weathered rocks from Callion gold deposit, Yilgarn Block, W.A.
S.M. Llorca. April, 1989. 10pp

- 58R Mineralogy and geochemistry of the Glasson gold deposit, Callion, Yilgarn Block, W.A.
S.M. Llorca. August, 1989. 33pp
- 73R Mineralogy and geochemistry of mineralised and barren felsic volcanic profiles, Parkinson Pit, Mt. Magnet, W.A.
K.M. Scott. September, 1989. 18pp
- 102R The petrography, mineralogy and geochemistry of weathering profiles developed on felsic, mafic, ultramafic and sedimentary rocks, Rand Pit, Reedy Mine, Western Australia.
I.D.M. Robertson, G.F. Taylor and M.A. Chaffee. December, 1990. Volumes I and II. 205pp
- 105R Mineralogy and geochemistry of soils overlying the Beasley Creek gold mine - Laverton, W.A.
I.D.M. Robertson. September, 1990. Volumes I and II 158pp (Joint report with Project 240)
- 109R Multi-element soil survey of the Mount Hope area, Western Australia.
M.J. Lintern, H.M. Churchward and C.R.M. Butt. May, 1990. 76pp
- 110R Gold morphology and composition at Panglo, Eastern Goldfields W.A.
K.M. Scott and J.J. Davis. April, 1990. 9pp
- 124R Morphology and geochemistry of particulate gold in the lateritic regolith, Mystery zone, Mt. Percy, Kalgoorlie, Western Australia.
A.Z. Gedeon and C.R.M. Butt. October, 1990. 41 pp
- 125R Hydrogeochemistry of the Panglo gold deposit.
D.J. Gray. October, 1990. 74pp
- 126R Chemistry of gold in some Western Australian soils.
D.J. Gray, M.J. Lintern and G.D. Longman. November, 1990. 62pp
- 127R The sorption of gold and silver on soil minerals.
D.J. Gray. December, 1990. 18pp
- 128R Chemistry of gold-humic interactions.
D.J. Gray, M.J. Lintern and G.D. Longman. November, 1990. 32pp
- 129R The distribution of gold and other elements in soils and vegetation at Panglo, Western Australia.
M.J. Lintern and K.M. Scott. October, 1990. 96pp
- 143R The mineralogical and geochemical effects of weathering on volcanics from the Panglo deposit, Eastern Goldfields, WA.
K.M. Scott. June, 1990. 47pp
- 147R Electron microprobe studies of minerals from weathered profiles, Parkinson Pit and environs, Mt. Magnet, WA.
K.M. Scott. July, 1990. 48pp
- 152R Multi-element dispersion in the saprolite at Beasley Creek gold mine, Laverton, Western Australia.
I.D.M. Robertson. April, 1991. Volumes I and II. 122pp

- 156R Geochemical dispersion in the regolith, Mystery Zone, Mt. Percy mine, Kalgoorlie, Western Australia.
C.R.M. Butt. January, 1991. Volumes I and II. 226pp
- 159R Distribution of gold and other elements in soils from the Mulline area, Western Australia.
M.J. Lintern and C.R.M. Butt. February, 1991. 56 pp
- 171R The mineralogical and geochemical effects of weathering on shales at the Panglo deposit, Eastern Goldfields, WA.
K.M. Scott. August, 1990. 35pp
- 178R The mineralogy and geochemistry of weathered mafic and ultramafic rocks, Parkinson Pit, Mt Magnet, Western Australia.
K.M. Scott and A. Martinez. October, 1990. 39pp
- 187R Geochemistry of the gossans, weathered mineralization and host rocks, Telfer gold mine, Western Australia.
J.R. Wilmschurst. March, 1991. Volumes I and II. 154pp

APPENDIX 2. SAMPLE PREPARATION, ANALYSIS AND QUALITY CONTROL

A2.1 INTRODUCTION

Although the analytical requirements of research and exploration are not necessarily the same, a statement of the procedures used by this project may provide a guide to those in exploration wishing to implement some of the multi-element techniques described herein. Geochemical research is dependant on accurate and precise analyses. No single analytical method or package could be expected to provide a panacea for the large number of elements (30-40) that were determined. After some investigation, a combination of largely non-destructive instrumental methods was selected which would attain the required standard and be cost-effective. Geochemical analysis is, in turn, dependant on the quality of sample preparation. Sample preparation was carried out entirely 'in house' because it could be adequately supervised.

A2.2 SAMPLE PREPARATION

Rock samples varied from 500-2000 g. These were jaw-crushed in Mn steel followed by tumble mixing on a plastic sheet. Some samples were spread thinly and 10-15 7-9 g portions were incrementally extracted to make up the 100 g aliquot used for milling. Others were progressively riffle-split to 100 g. Contamination from jaw-crushing is negligible compared to that introduced by milling. For all splitting and handling, only plastic implements were used and all equipment was thoroughly cleaned by air-blowing between samples. The 100 g aliquots were ring-milled and all mill components were wiped with ethanol between samples.

Sample contamination from mill materials is inherent when any sample is pulverized. There are two ways to minimize this. Either a mill is used which is made of a material that is not included in the analytical scheme or of a material which is already present in excess (in which case the contamination is camouflaged). High Cr steel and tungsten carbide mill materials were excluded as Cr, Co and W were to be included in the analytical scheme. Agate was tried but the milling time was inordinately long and the light agate puck was unable to crush some hard, granular materials. Ketos steel (C 0.9%, Si 0.3%, Mn 1.35%, Cr 0.5%, W 0.5%) was used initially but later a special mill was constructed of case-hardened K1045 steel (Robertson and Crabb, 1988). Maximum estimated contamination from the mill, relative to a highly abrasive 100 g quartz charge, is given in Table A2.1 (Robertson *et al.*, 1989). Actual contamination of a much softer saprolitic material is probably less by half to one order of magnitude. The contaminating elements, chiefly Fe, Mn, Cr, Cu and Ni, generally would be at less than their natural abundances by one or two orders of magnitude so any contamination is effectively camouflaged. The North Ryde laboratory used a Kite steel mill (C 1%, Mn 2%, Si 0.3%). Contamination levels for Ketos and Kite mills have not been as thoroughly investigated as K1045. It is *estimated* that maximum contamination (relative to quartz) for Ketos steel would be 80 ppm Mn, 30 ppm Cr and 30 ppm W; for Kite steel 132 ppm Mn.

A2.3 GEOCHEMICAL ANALYSIS

A2.3.1 Geological materials

As sample dissolution by most techniques (except perhaps by fusion or HF-teflon bomb) tends to be incomplete for some materials, non-destructive instrumental techniques were preferred. The highly varied nature of weathered rocks necessitates techniques where matrix corrections can be applied with confidence. The analytical package that was employed for the bulk of the work is given in Table A2.2.

Table A2.1 Steel analysis and estimated contamination for K1045 ring mill

Element	Steel (%)	Max Contamination ppm
Ag	<0.0010	<0.07
As	0.0005	0.04
Ba	<0.002	<0.15
Bi	<0.0010	<0.07
Cd	<0.0002	<0.015
Co	0.0071	0.5
Cr	0.0795	5.5
Cu	0.0850	6.0
In	<0.000	<0.035
Mn	0.6592	45.0
Mo	0.0260	2.0
Nb	0.0220	1.5
Ni	0.0620	4.5
Pb	0.0020	0.15
Sb	0.0025	0.2
Sn	0.0080	0.6
Ta	<0.010	<0.7
Ti	0.0045	0.3
V	0.0040	0.3
W	<0.002	<0.15
Zn	0.0030	0.2

The bulk of the analytical work was generated at Floreat Park. Here, X-ray fluorescence analysis on pressed powders, using a Philips PW1220C, coupled with some INAA analysis (Becquerel Laboratories) comprised the main part of the trace element package. Initially Au determinations were by cyanide digestion, followed by ICP/MS or Graphite Furnace-AAS, before the INAA package, which includes Au, was initiated. Although XRF fused disc analysis would have been preferable for most major elements, in-house facilities were not available at Floreat Park, so most of the major elements were determined by ICP analysis on a Hilger E-1000, following Li metaborate fusion and dissolution in dilute HNO_3 . This analytical package needed to be complemented by some ICP/MS analysis (Analabs) due to the very low abundances of some critical elements. Samples for ICP/MS analysis were dissolved in HClO_4 - HNO_3 -HF. AAS analysis was used for the determination of Li, and some Na and K. Gravimetry was used to determine losses on ignition and drying, the latter showing a particularly poor precision due to variable uptake of moisture by smectites.

At North Ryde, major elements were determined by XRF analysis on a Siemens SR1 after fusion with Li metaborate, La oxide and Na nitrate. Trace elements were determined by ICP analysis on a Labtam V-25 after dissolution using HF, HNO_3 and HClO_4 . Gold, As and Sb were determined by INAA.

Some minor difficulties, peculiar to weathered rocks, were encountered with the preparation of pressed discs. Initially boric acid-backed discs were used. Smectite-rich samples tended to expand, distorting the discs and making them difficult to fit in the holder. These clays later dehydrate under vacuum, the disc material and its backing separate and the disc, which is inverted during irradiation, tends to fall out. This was largely overcome by making un-backed, self-supporting discs with PVA glue (0.5% dry) which necessitated oven

drying the disc. Although these were more stable, the drying introduced an additional difficulty. Soluble salts, especially Na, tend to migrate and gather at the disc surface during drying, giving unusually high results.

A2.3.2 Biological materials

Major and trace elements were determined on washed plant and mull material by ashing, digesting the ash in aqua regia and analysing on a Hilger E-1000 ICP. Gold was either extracted with DIBK from an aliquot of the ICP digest solution and determined by graphite furnace-AAS or, with other elements, was determined by direct INAA analysis of pressed, dry material (Becquerel Laboratories). Difficulties were encountered with INAA analysis of some samples from Panglo (Report 129R). The high salt content caused a severe interference with Au, resulting in unacceptably high detection limits, so the alternative wet chemical method was used instead.

A2.3.3 Groundwaters

Samples were from generally uncased boreholes of low hydrological transmissivity, where a pump could not be used. High Fe abundances in some waters caused substantial precipitation of Fe oxyhydroxides on oxidation. It was necessary to analyse some metals, such as Au, to low detection limits but the high salinity (> seawater) of these groundwaters caused some analytical difficulties. After collection using a pump sampler (Hart et al., 1985), the samples were filtered and acidified in the field to prevent precipitation. In the laboratory, Au and pathfinder elements were preconcentrated on activated carbon. The chalcophile and pathfinder metals were determined by ICP (Hilger E-1000), calibrated with standards matched to the salinities of the samples. The major cations were determined by AAS, anions by ion chromatography and Au by carbon furnace-AAS. A summary of groundwater analyses methods is given in Section 2 of Report 125R.

A2.4 STANDARDS

A suite of seven widely varied weathered rock standards were collected, pulverized and homogenized in a 'V' blender (about 30 kg each). At Floreat Park, aliquots of these were introduced into the analytical sequence at a frequency of 1:10 to 1:50 to monitor precision and detect any significant batch errors. As far as possible, the standards were matrix-matched to the materials being analysed. Apart from their monitoring functions, use of such standards throughout improve the reliability of comparisons between data sets, facilitating later multivariate analysis of combined data. Random ordering of samples in the analytical system was used in some studies as an added precaution.

Table A2.2 Analytical methods and detection limits

INAA		XRF		ICP/MS		ICP		AAS	
As	2	Ba	15	Ag	0.1	Al ₂ O ₃	0.1	K ₂ O	200
Au	0.005	Cu	5	Bi	0.1	CaO	0.1	Li	2
Br	2	Fe	1000	Cd	0.05	MgO	0.1	Na ₂ O	2
Ce	2	Ga	5	In	0.05	Na ₂ O	0.6		
Co	1	Ge	3	Sn	0.1	P ₂ O ₅	0.1		
Cr	5	Mn	20			SiO ₂	0.1		
Cs	1	Na	100			Ba	100		
Eu	0.5	Na ₂ O	500			Be	5		
Fe	500	Nb	5			Co	1		
Hf	1	Ni	10			Cr	100		
Ir	0.02	Pb	5			Cu	100		
La	0.5	Rb	5			Fe ₂ O ₃	0.1		
Lu	0.2	S	50			Mn	100		
Mo	5	Se	2			Ni	50		
Sb	0.2	Sr	3			TiO ₂	0.1		
Sc	0.1	Ti	100			V	100		
Sm	0.2	V	10			Zr	100		
Ta	1	Y	3						
Th	0.5	Zn	5						
U	2	Zr	4						
W	2	Ag	5						
Yb	0.5	As	7						
Ag	5	Bi	7						
Ba	100	Cd	5						
K	2000	Co	5						
Na	100	Cr	5						
Rb	20	Cs	7						
Se	5	In	5						
Zn	100	La	10						
		Nd	10						
		Sb	5						
		Sc	7						
		Sn	5						
		Ta	7						
		Th	7						
		U	7						
		W	7						

Elements in bold type constitute the preferred geochemical package.