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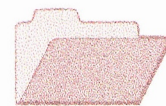
Cooperative Research Centre for  
Landscape Evolution & Mineral Exploration



**CSIRO**  
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**OPEN FILE  
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# **INVESTIGATIONS OF THE HYDROGEOCHEMICAL DISPERSION OF GOLD AND OTHER ELEMENTS AT LAWLERS, WESTERN AUSTRALIA**

## **Volume I**

*D.J. Gray*

**CRC LEME OPEN FILE REPORT 91**

**January 2001**

**(CSIRO Division of Exploration and Mining Report 26R,  
2nd Impression.)**

CRC LEME is an unincorporated joint venture between The Australian National University, University of Canberra, Australian Geological Survey Organisation and CSIRO Exploration and Mining, established and supported under the Australian Government's Cooperative Research Centres Program.





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## RESEARCH ARISING FROM CSIRO/AMIRA YILGARN REGOLITH GEOCHEMISTRY PROJECTS 1987-1996

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" 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 commenced with 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 (1991-1993).** 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.

Most reports related to the above research projects were published as CRC LEME Open File Reports Series (Nos 1-74), with an index (Report 75), by June 1999. Publication now continues with release of reports from further projects.

### **P252: Geochemical exploration for platinum group elements in weathered terrain.** Leader: Dr C.R.M. Butt.

This project was designed to gather information on the geochemical behaviour of the platinum group elements under weathering conditions using both laboratory and field studies, to determine their dispersion in the regolith and to apply this to concepts for use in exploration. The research was commenced in 1988 by CSIRO Exploration Geoscience and the University of Wales (Cardiff). The Final Report was completed in December 1992. It was supported by 9 companies.

### **P409: Geochemical exploration in areas of transported overburden, Yilgarn Craton and environs, WA.**

Leaders: Drs C.R.M. Butt and R.E. Smith.

About 50% or more of prospective terrain in the Yilgarn is obscured by substantial thicknesses of transported overburden that varies in age from Permian to Recent. Some of this cover has undergone substantial weathering. Exploration problems in these covered areas were the focus of Project 409. The research was commenced in June 1993 by CSIRO Exploration and Mining but was subsequently incorporated into the activities of CRC LEME in July 1995 and was concluded in July 1996. It was supported by 22 companies.

Although the confidentiality periods of Projects P252 and P409 expired in 1994 and 1998, respectively, the reports have not been released previously. CRC LEME acknowledges the Australian Mineral Industries Research Association and CSIRO Division of Exploration and Mining for authority 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.

This report (CRC LEME Open File Report 91) is a second impression (second printing) of CSIRO, Division of Exploration and Mining Restricted Report 26R, first issued in 1994, which formed part of the CSIRO/AMIRA Project P409.

#### **Copies of this publication can be obtained from:**

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## PREFACE

The CSIRO-AMIRA Project "Exploration in Areas of Transported Overburden, Yilgarn Craton and Environs" (Project 409) has, as its principal objective, development of geochemical methods for mineral exploration in areas with substantial transported overburden, through investigations of the processes of geochemical dispersion from concealed mineralization. The Project has two main themes. One of these, *'Surface and subsurface expression of concealed mineral deposits'* is addressed by this report, which focuses on the hydrogeochemistry of the Lawlers district.

Hydrogeochemistry has long been considered as having considerable potential in exploration, on the premise that groundwaters are a pervasive medium by which ore-associated elements may be widely dispersed and thus present a broader target than the mineralization itself. This target may be relatively localized, indicating mineralization just missed by drilling, or be of district or regional scale. Prospective zones of high reactivity, such as shears and faults, may also have distinct hydrogeochemical signatures, though the rocks themselves may have unremarkable compositions. In addition, hydrogeochemical studies may provide information on currently active processes of weathering. Despite its potential, however, hydrogeochemical exploration has proved difficult to apply, largely due to the complex element interactions and the strong influence of the local environment on the salinity, pH, composition and hydrology of the groundwater.

The Lawlers district contains several Au deposits, located in both residual and transported areas. It therefore represents a field area where the hydrogeochemistry of these different environments can be compared. Mineralization in residual areas are situated in relict and erosional regimes, characterized by outcropping lateritic duricrust and subcropping ferruginous saprolite. In the depositional areas, complete and partly truncated profiles are overlain by accumulations of detritus derived by erosion of the laterite profile, reaching up to 30 m in thickness. Hardpan is common throughout the study area. The groundwaters are neutral and of low salinity and provide a further comparison, with the acid and/or saline groundwaters of the southern Yilgarn Craton. A most surprising aspect of the results has been the high concentration of dissolved gold in some groundwaters. However, these are confined to the mineralised systems and display little or no dispersion.

C.R.M. Butt and R.E. Smith,  
Project Leaders.  
August, 1994



## ABSTRACT

The hydrogeochemistry of the Lawlers district was investigated, with a view to understanding the interaction of groundwaters with mineralized rocks, and the potential for exploration, particularly in areas of extensive overburden. Groundwaters at Lawlers are neutral, with a similar Eh range to other neutral groundwaters. However, they differ from groundwaters investigated at other Yilgarn sites in having low salinities and marked divergence from sea water ratios, suggesting that the major ion concentrations are strongly controlled by local lithological or hydrological factors. Elements that appear to be controlled by mineral equilibration in some or all groundwaters are Ba (barite equilibration), Ca, Mg and  $\text{HCO}_3$  (carbonate), Mn (rhodochrosite), Sb [ $\text{Sb}(\text{OH})_3$ ], Pb and V ( $\text{Pb}_2\text{V}_2\text{O}_7$ ).

The most marked feature of the Lawlers groundwaters is the extremely high Au concentrations, with the highest observed concentration of 40  $\mu\text{g/L}$  being about ten times greater than any other previously reported values. These high concentrations are correlated with highly anomalous Co concentrations at Hidden Secret and in the Gt. Eastern/Caroline pits area but not at Genesis. Under the groundwater conditions observed at Lawlers, the most likely mechanism for dissolution is expected to be as the thiosulphate complex  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ . The generation of thiosulphate requires oxidation of sulphides to occur under neutral conditions, with the acidity produced being neutralized by the dissolution of minerals such as primary carbonates. This is consistent with limited results at Hidden Secret suggesting that higher Au concentrations are correlated with increased Mg, Ca,  $\text{HCO}_3$  (from carbonate dissolution) and  $\text{SO}_4$  (from sulphide oxidation).

Most of the specific sites investigated showed specific groundwater element anomalies:

- (i) Hidden Secret - Au, TDS,  $\text{SO}_4$ , P, Mn, Fe, Co, Ni, Y, REE, W, As, Sb, I, U, and possibly Ba, Ga, Sc and Ge;
- (ii) Genesis - Au, Sc, As, and possibly Ni and Sb;
- (iii) mineralization at Gt. Eastern/Caroline - Au, Co, and possibly  $\text{SO}_4$ , Sc and As;
- (iv) mineralization at Four Corners -  $\text{SO}_4$ , Al, Ga, Mn, Fe, Co, Ni and Mo (though generally based on only one sample at the centre of the mineralized area);
- (v) granitic rocks at Gt. Eastern/Caroline - Al, Ga, Ba, Mn, Mo and U;
- (vi) ultramafic rocks - Cr, Cs and Sr;
- (vii) southern part of Four Corners - TDS, B, Sr,  $\text{HCO}_3$ , I and U (possibly indicating a different groundwater system in this area);

The differences in the minor element 'signatures' for the groundwaters in areas of major Au mineralization (Genesis, Gt. Eastern/Caroline, Hidden Secret) may reflect differences in the lithologies of the three sites and/or the geochemistry of the Au mineralization. The Gt. Eastern/Caroline and Hidden Secret groundwaters have groundwater signatures similar to other mineralized sites elsewhere in the Yilgarn, with anomalies in a range of chalcophile and other pathfinder elements. In contrast, groundwaters at Genesis are anomalous in only Au, Sc and As, possibly due to the Genesis ore deposit being hosted in a quartzite unit with free-milling Au and disseminated arsenopyrite.

At the Four Corners area, which is covered with extensive transported overburden, there are anomalous concentrations of varying elements (but not Au), with size of the groundwater anomaly appearing to be less than 250 m diameter. The exception to this is  $\text{SO}_4$ , which has a more disperse anomaly.

Groundwater at Lawlers appears to have exploration potential, particularly in the residual areas. In areas of extensive transported overburden, there is no observed groundwater Au response, though some elements ( $\text{SO}_4$ , Ga, transition metals, Mo) may have potential as pathfinders for Au.

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# 1 INTRODUCTION

Research work in Australia and elsewhere (Morris, 1982; Hamilton *et al.*, 1983; Giblin and Snelling, 1984; Runnells, 1984; Dissanayake and Weerasooriya, 1986; Hall *et al.*, 1986; McHugh, 1988; Bergeron and Choinière, 1989; Dekkers *et al.*, 1989; Cidu and Edmunds, 1990) has suggested that hydrogeochemistry may be useful for exploration for Au and other metals. Although many such investigations have been undertaken in areas with a dominantly residual regolith, it is feasible that groundwater may also provide a useful exploration medium in areas of extensive transported overburden.

A primary justification given for the use of hydrogeochemistry in mineral exploration is that groundwater anomalies may be broader and more regular than the mineralization and secondary dispersion halo in the regolith, thus enhancing the exploration signature. In addition, areas of high reactivity (*e.g.*, faults and shear zones) may have distinct hydrogeochemical signatures even where they are unremarkable in terms of elemental abundances, and where normal drilling makes petrographic study difficult. However, such effects may also be counter-productive, as interpretation may become complicated by the various factors.

Hydrogeochemical studies also have value in providing information on how various materials are weathering, thereby enhancing understanding of active dispersion processes and assisting in the development of weathering and geochemical models, which are essential for effective exploration in regolith dominated terrain.

The aims of the Lawlers hydrogeochemical project were, therefore:

- (i) to provide information on whether groundwater can be used successfully as an exploration medium in the Lawlers district, and if so, how it could be done most effectively and economically;
- (ii) to yield data on geochemical dispersion processes;
- (iii) to contribute to a groundwater database on the characteristics of groundwaters at various sites, and to enhance our understanding of groundwater processes in mineralized zones.

The Lawlers area holds considerable interest for hydrogeochemical investigations for a number of reasons:

- (i) it lies north of the Menzies line, in the eastern Yilgarn, in an area of extensive hardpan;
- (ii) groundwater salinity is very low. This is in contrast with Granny Smith, the other site north of the Menzies line investigated as part of AMIRA Project 409, permitting comparison of the effect of salinity differences on the chemistry of Au and other elements;
- (iii) groundwater investigations are complementary to other studies conducted by CSIRO at this site (Anand *et al.*, 1991, 1993).

The scope of this investigation includes the effect of underlying lithology on the observed water chemistry, thermodynamic modelling, mapping of the data and comparison with results from other Yilgarn sites.

## 2 SITE STUDY AND METHODS

### 2.1 Site characteristics

#### 2.1.1 Location

The Lawlers study area is 300 km north of Kalgoorlie (Figure 1) and spans the boundary between the Sir Samuel (SG-51-13) and Leonora (SH-51-01) 1:250,000 map sheets. Access is gained from the sealed Leonora-Leinster road or by the unsealed road from Sandstone to the Agnew townsite.

#### 2.1.2 Geology

The district lies within the Agnew supracrustal belt in the Archaean Yilgarn sub-province. The Lawlers Greenstone Sequence is up to 3 km thick. It consists of interlayered basalt, high-Mg basalt, ultramafic rock, gabbro and differentiated gabbro-pyroxenite-peridotite sills, and thin fine-grained sedimentary and silicic volcanogenic layers (Platt *et al.*, 1978). The gabbroic sills are up to 300 m thick, concordant and laterally very extensive. Volcanic and sedimentary units are interlayered with sills throughout. The sequence is intruded by tonalite. The Lawlers Anticline, a major north plunging upright fold, (Figure 2), which is the most prominent structural feature in the area, lies in this sequence. A later leucogranite has been mapped in the area (Partington, 1986) cutting both the tonalite and greenstones.

The Lawlers Greenstone Sequence is overlain on the west side of the Lawlers Anticline by the Scotty Creek Sedimentary Sequence (Figure 2A). This is about 1500 m thick and consists of basal conglomerate derived from mafic and ultramafic units within the Lawlers Greenstone Sequence (Platt *et al.*, 1978). The Scotty Creek Sequence faces westwards and grades into quartz-felspathic sandstones with tonalitic clasts and sporadic chert and shale horizons.

North and east of Lawlers, the Lawlers Greenstone Sequence is also overlain by the Vivien Sedimentary Sequence of sandstone, siltstone, shales, conglomerates, and cherts. Cudahy (personal communication) considers the Vivien Sequence to be stratigraphically equivalent to the Scotty Creek Sequence. Partington (1986) and Eisenlohr (1989) have argued that the Scotty Creek Sequence has an angular unconformable relationship with the Lawlers Greenstone Sequence.

West of the Scotty Creek Sequence lies the Waroonga Gneiss. The contact lies within a major ductile shear zone (Waroonga Shear zone), and the original relationship of the gneiss to the supracrustal sequence is not clear.

A generalized geological map of the study area, with positions of water samples, is shown in Figure 3.

#### 2.1.3 Mineralization

The Au deposits in the Lawlers district generally fall into the following broad categories.

- (i) Disseminated Au within alteration haloes  $\pm$  quartz vein systems in shear zones (*e.g.*, Great Eastern, McCaffery and Turrett). Most of these deposits occur in shear zones and are in excess of 100 m long and 100 m deep. The host rocks are commonly extensively affected by potassic metasomatism (resulting in sericitization and biotitization) and intense carbonatization. Centrally, pyrite  $\pm$  arsenopyrite alteration is dominant but is restricted to 1-5 m from the shear zones. Gold is strongly concentrated in the pyritic alteration zones. The lithology and chemistry of the host rocks influence the position of the shear zone and the Au grade.
- (ii) Laminated Au-bearing quartz veins in fractures or shear zones. These generally form in tensional structures developed in brittle mafic host rocks associated with major movement along the Waroonga shear zone (Partington 1986). The quartz veins are persistent, with 1-10 m thick veins extending over a strike length of over 1 km and to depths of over 250 m. The laminated veins consist almost exclusively of quartz, with thin bands of chlorite and



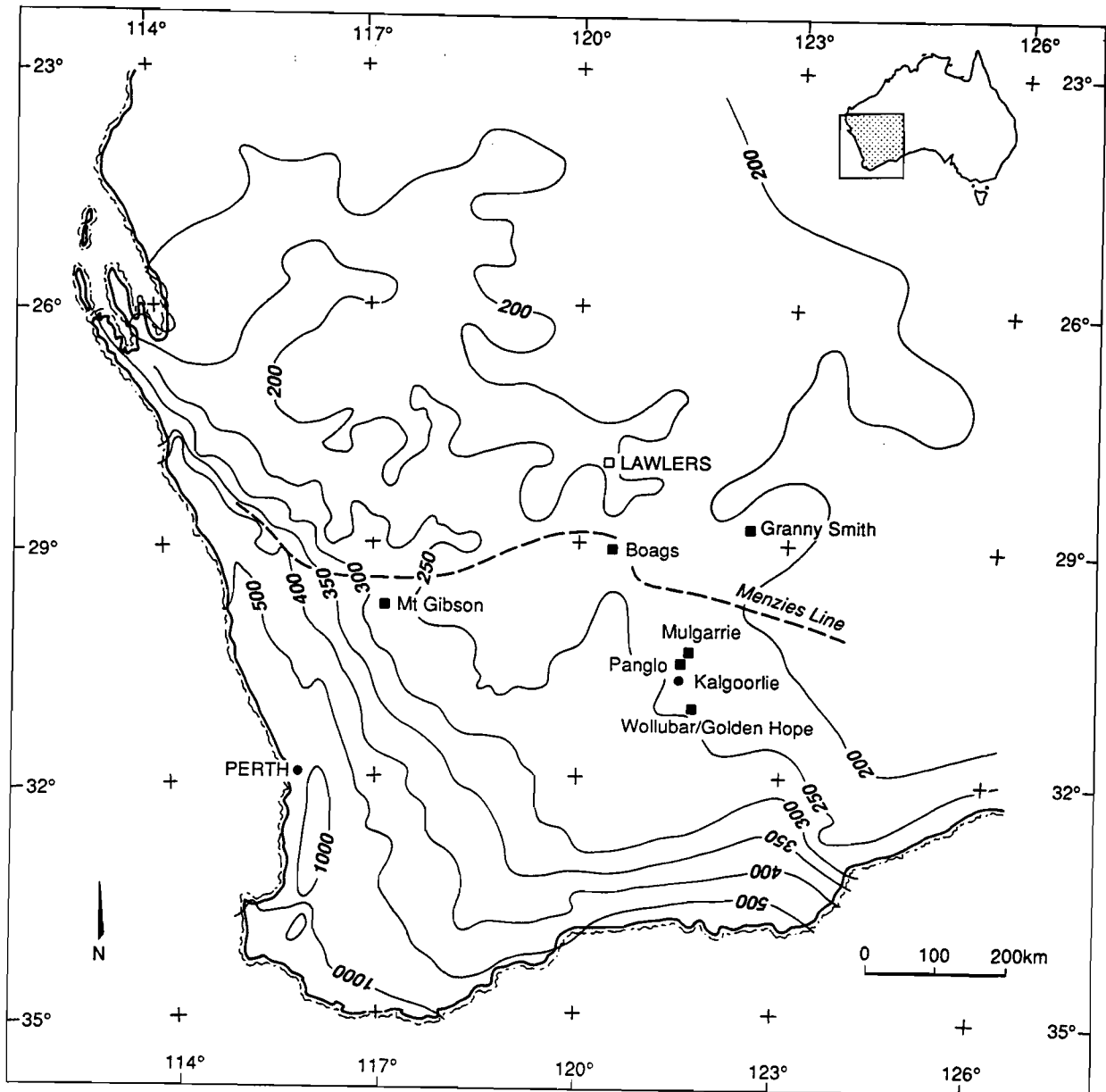


Figure 1: Regional map of southwest Australia, showing location of the Lawlers study area, and of other sites referred to in this report.

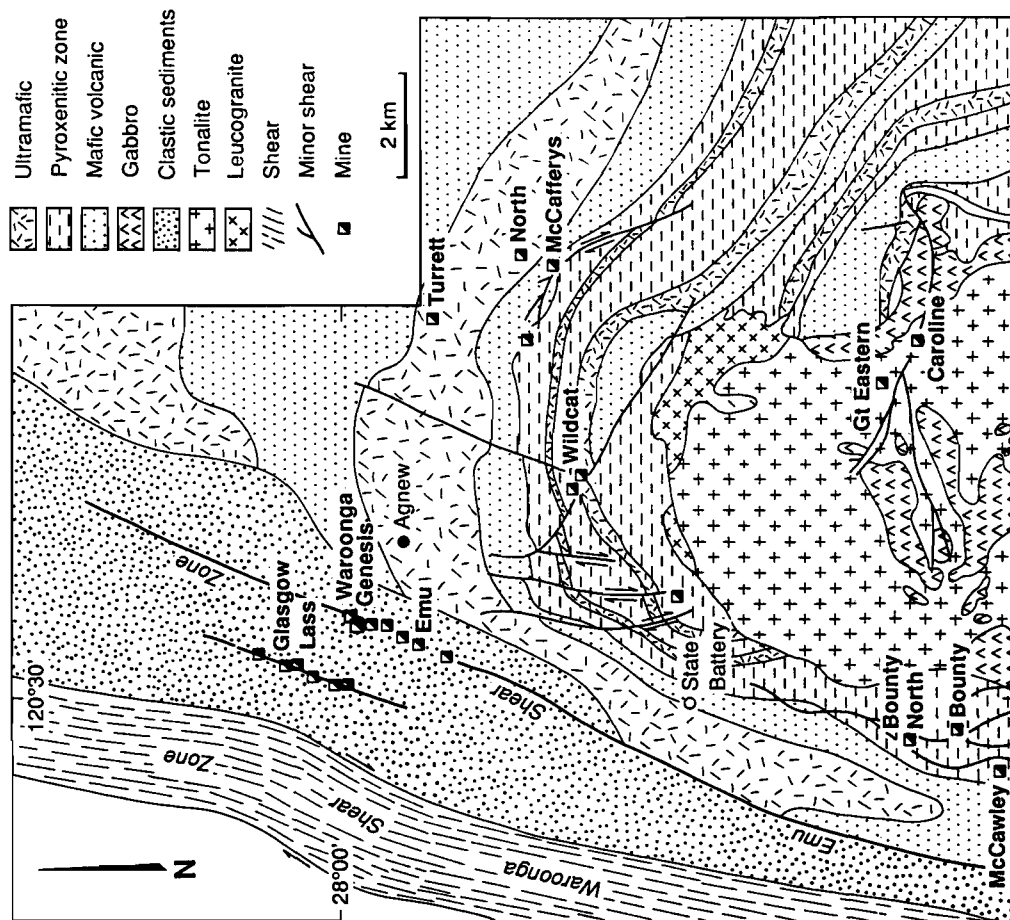


Figure 2B: Detailed geology in the vicinity of Lawlers

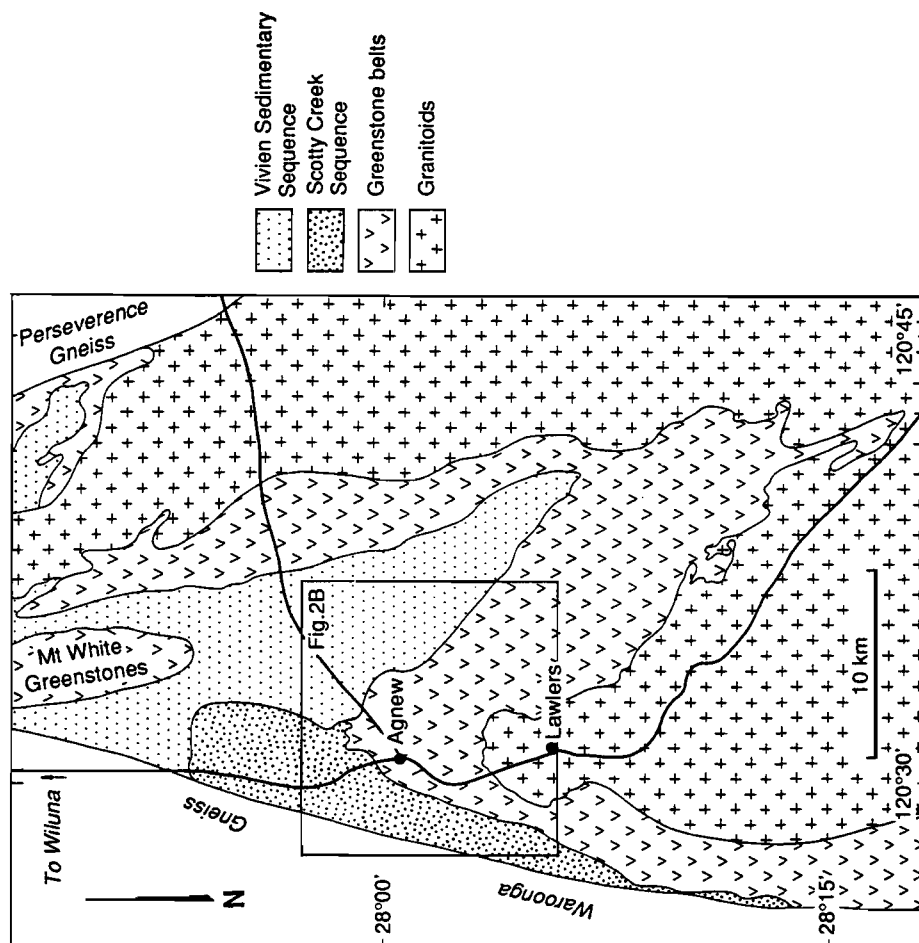


Figure 2A: Regional geology of the Lawlers region  
(after Platt *et al.*, 1978)



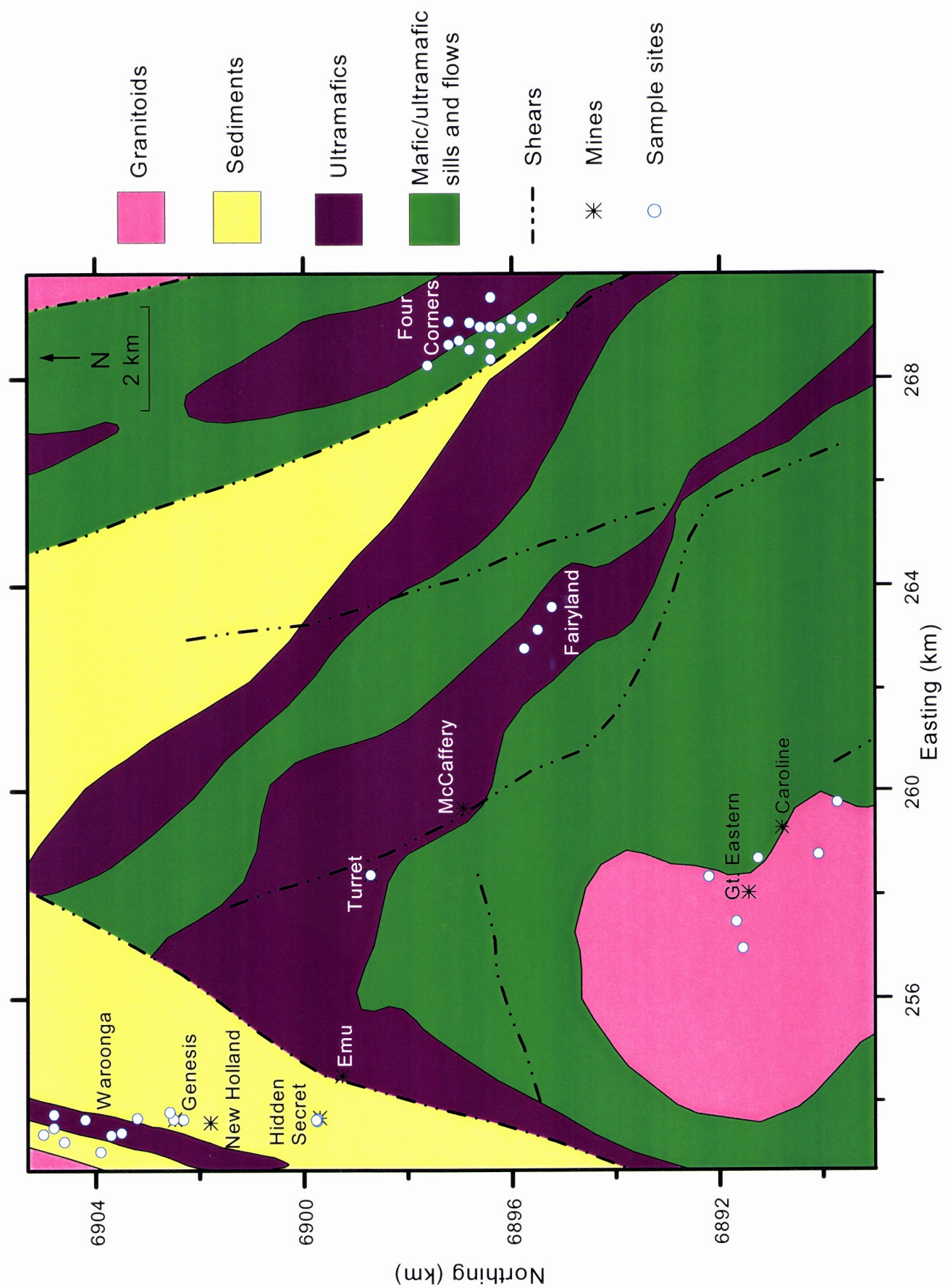


Figure 3: Generalized geological map of the Lawlers study area, with water sampling locations.



low concentration of Fe sulphides. Free Au may be present in the veins. The contained Au lodes are generally small in extent but rich in Au.

- iii) Altered and sulphidic shoots with little or no quartz in major shear zones (*e.g.*, Emu). Gold mineralization is confined to the major sheared contact (Waroonga shear) of the Scotty Creek Sequence and the underlying Lawlers Greenstone Sequence. There is almost a total absence of quartz veining and the higher Au grades may be associated with biotite alteration. Alteration assemblages are variable but include sulphides (pyrite, pyrrhotite,  $\pm$  arsenopyrite), quartz, carbonate, actinolite, and chlorite. The Au is very fine grained at the Redeemer deposit and not associated with sulphides. Structural zones cross cutting the main Waroonga shear and the chemistry of the host rocks within the ductile shear zones are thought to be important influencing factors.
- iv) Quartz stockworks and ladder veins in metasediments (*e.g.*, Genesis). The Au mineralization is hosted in a quartzite unit of the Scotty Creek Clastic Sequence, within thin sets of quartz veins. Although arsenopyrite is disseminated throughout the ore body, Au is only rarely associated with it.

Gold derived from any of the four primary sources has been redistributed by weathering, with secondary concentrations occurring in the saprolite and, in places, in the overlying lateritic residuum. This secondary Au mineralization is, in effect, a further style of mineralization and has importance as low to medium tonnages of low-grade Au resources can be defined.

#### 2.1.4 *Geomorphology and Drainage*

The Lawlers district is situated on the Great Plateau of Western Australia (Jutson, 1950). It is a broadly-undulating terrain with scattered belts of hills providing some local relief. More detailed relief variation, such as at breakaway scarps, is the result of differential stripping of the extensive deeply-weathered mantle and by localized deposition of detritus resulting from this process.

This district straddles a divide between the Lake Raeside drainage to the south and that of Lake Miranda and Lake Darlot to the north. For much of its length, the northwest-oriented divide comprises the crests of prominent breakaways, the Agnew Bluff. Extensive erosional tracts extending south from these breakaways are first dominated by hill belts, whereas, north of the divide, the topography is dominated by long, very gentle, smooth slopes. Many of these have their origin on the broadly convex, laterite-mantled crests, immediately above the Agnew breakaway, and gradually merge down to broad alluvial floors of tributary valleys and thence to the main drainage sumps of Lake Darlot and Lake Miranda. The direct length of this drainage is approximately 60 to 70 km, and the southward drainage is from 20 to 30 km. Alluvial floors, often associated with a complex of minor meandering channels, are little incised below the main alluvial plain and the drainages commonly terminate on sandplain tracts over granitic rocks. A simple geomorphological map of the study area is given in Figure 4.

#### 2.1.5 *Regolith relationships*

The form and degree of truncation was studied in detail in Anand *et al.* (1991). The top of the residual profile is composed of a layer of lateritic residuum averaging some 3 to 8 m in thickness, comprising a sub-unit of loose pisoliths and nodules which may be underlain by a sub-unit of nodular duricrust. A zone of ferruginous saprolite characterized by bodies of iron segregations generally underlies the lateritic residuum. It is established that ferruginous saprolite forms a blanket deposit up to several metres thick in many areas in the Lawlers district and is preferentially developed over mafic and ultramafic lithologies. In turn, ferruginous saprolite grades into a thick clay-rich saprolite, that extends to vertical depths of 50 to 70 m.

Development of many nodules and pisoliths in lateritic residuum is associated with fragmentation of ferruginous saprolite. Fragmentation of bodies of iron segregations can also yield nodules and pisoliths that become incorporated within the lateritic residuum. The Fe-rich duricrusts are probably formed by



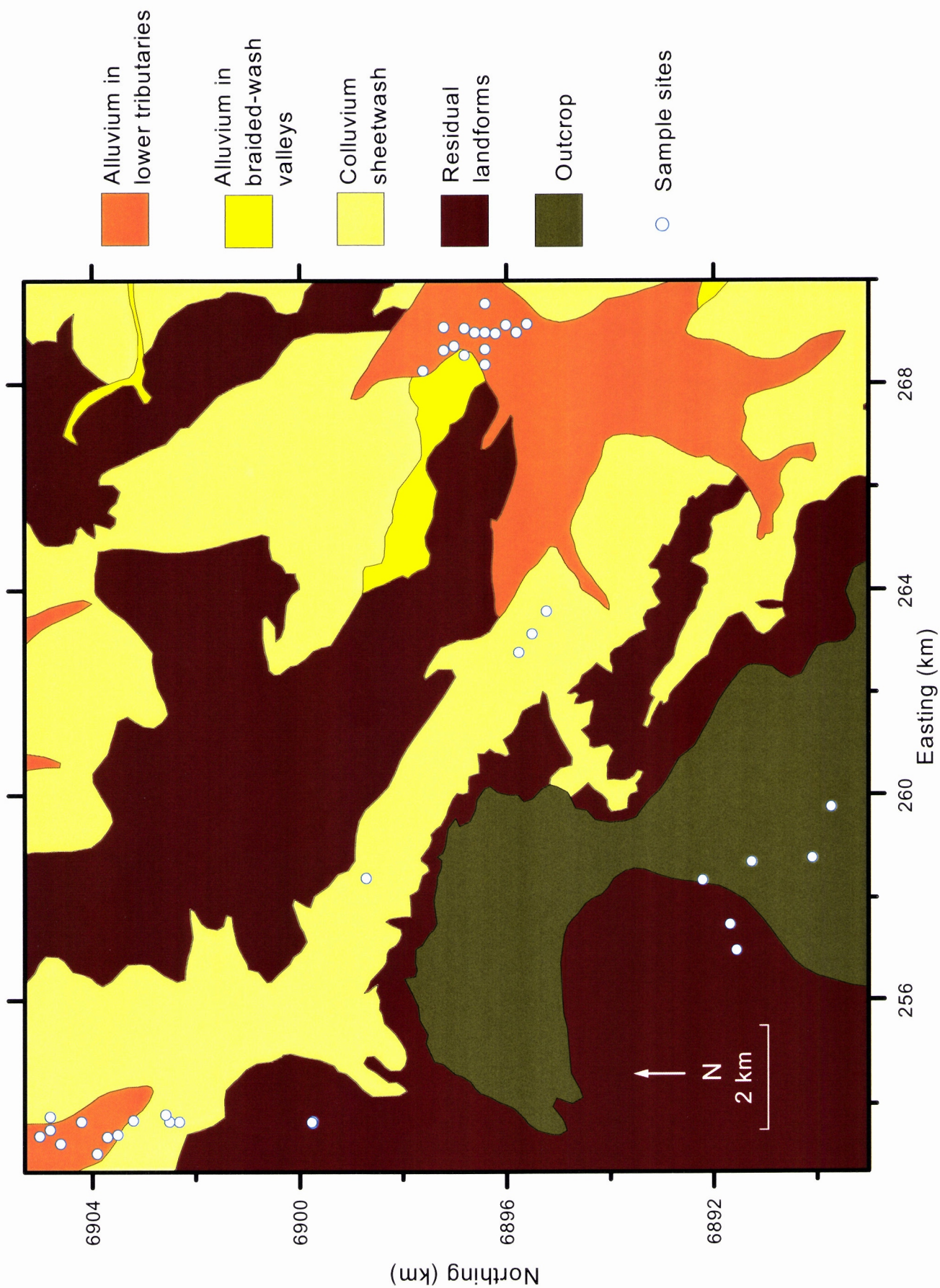


Figure 4: Simple geomorphological map of the Lawlers study area (after Anand *et al.*, 1991), with water sampling locations.

absolute accumulation of Fe, possibly as impregnations of soils/sediments in local valleys, which now occur as ridge crests in the present landscape because of inversion of relief.

Recent cementation of *in situ* regolith and detritus resulting from the erosional modification of the old surface by Si and Fe has formed hardpan as an almost ubiquitous near-surface horizon.

The regolith patterns observed in the Lawlers district are explained in terms of the distribution of:

- (i) regimes of erosion of the laterite profile to the level of saprolite, saprock or bedrock, resulting in terrain characterized by low hills;
- (ii) regimes where the essentially-complete laterite profile is preserved, commonly forming gentle ridge crests and backslopes;
- (iii) regimes characterized by depositional accumulations of detritus derived by erosion of the laterite profile, burying the partly-truncated, and in places complete, laterite profile in the lower slopes of colluvial/alluvial outwash plains. In the depositional areas, the sediments reach up to 30 m in thickness.

Buried residual laterite profiles are widespread beneath the colluvium and alluvium. Distribution of transported material is controlled by the outcrop associated with the anticline (compare Figures 3 and 4) with deeper alluvium associated with a northward drainage channel in the east of the study area (Four Corners) and a smaller drainage system in the northwest of the study area (Waroonga).

The soils occurring within those truncated regimes that have mafic or ultramafic bedrock are predominantly red light clays and sandy clay loams. They are commonly acidic and underlain by red-brown hardpan. The red clays commonly contain pseudomorphic grains after amphiboles, further evidence of their mafic origin. The occurrence of pedogenic calcrete at shallow depths in the erosional regimes generally relates to a mafic lithology. Soils on felsic lithologies are acidic, yellowish-brown, sandy loams. Residual regimes are dominated by acidic, brown gravelly sandy loams and sandy clay loams and generally without red-brown hardpan. The soils developed in the colluvium/alluvium of the depositional regimes are acidic, gravelly sandy clay loams and light clays.

#### 2.1.6 Climate

The study area has a hot, arid climate with an unreliable median annual rainfall of approximately 200 mm. Rain can fall in both summer and winter, but the highest incidence tends to be in late summer resulting from rain-bearing depressions, dependent on cyclonic activity. The mean daily maximum temperature for January is 36° and that for July is 18° (Gentilli, 1971). Frosts are frequent in winter.

#### 2.1.7 Vegetation

The area is characterized by sparse low acacia woodlands with mulga (*Acacia aneura*) being the dominant species. The shrub layer is dominated by poverty bush and turpentine (various *Eremophila* sp.) and rattle bush (various *Cassia* sp.). More shrubby examples of the same species dominate the hill tracts with their shallow, stony soil.

### 2.2 Sample collection, treatment and analysis

Groundwaters were sampled at various times from 1991 to 1993, in several parts of the Lawlers district (Figures 3 and 4). These samples are divided into 8 groups:

- (i) Fairyland: sampled from pumping bore in the Fairyland borefield;
- (ii) Genesis: seeping and upwelling groundwaters from the Genesis pit;
- (iii) Gt. Eastern/Caroline: groundwaters in the vicinity of Gt. Eastern and Caroline pits (also close to the Lawlers mill and tailings dam);

- (iv) Hidden Secret: groundwaters from bore holes at the base of the Hidden Secret pit;
- (v) Waroonga: drill holes north of Genesis pit;
- (vi) Four Corners south: drill holes in the southern part of the four corners area;
- (vii) Four Corners north: drill holes in the northern part of the four corners area;
- (viii) Turrett: sampled from a seepage pond at the base of the Turrett pit.

The groundwater samples in each group are given in Table 1. Groundwaters from groups (iii) to (vii) were bailed from open drill holes using a pump-sampler. Group (i) represents an unmineralized area; groups (ii) - (iv) are sampled from within or close to mineralized rocks; and groups (v) and (vi) are groundwaters from areas of transported overburden. Analysis of the data suggests that the Four Corner groundwaters are divided into two groups: the four southern-most samples, with higher salinities and higher concentrations of various elements (Table 2; Sections 4.1 and 4.2), and the remaining 11 samples further north; for this reason these two groups are plotted and discussed separately in later sections. The Turrett sample was taken from ponded water from the bottom of the pit and the elemental composition of this sample was not considered representative of the groundwater (with the exception of most of the major ions, which should not be affected by prolonged exposure to air).

Table 1: Groundwater sample groups.

Group	Sample Numbers
Fairyland	Law1-2, Law12
Genesis	Law3-4, Law13
Gt. Eastern/Caroline	Law5-10
Hidden Secret	Law14-16
Waroonga	Law17-19, Law35-40
Four corners - south	Law20-23
Four corners - north	Law24-34
Turrett	Law11

Waters were analysed for pH, temperature, conductivity and oxidation potential (Eh) at the time of sampling. A 125 mL water sample was collected in a polyethylene bottle (with overfilling to remove all air) for later  $\text{HCO}_3^-$  analysis by alkalinity titration in the laboratory. Following this, about 1.5 L of water was filtered through a 0.2  $\mu\text{m}$  membrane filter in the field. About 100 mL of the filtered solution was acidified [0.1 mL 15 moles/litre (M) nitric acid ( $\text{HNO}_3$ )], and analysed for Cu, Pb and Cd by Anodic Stripping Voltametry (ASV) at CSIRO Floreat Park Laboratories, for Al, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P/I (distinction between P and I is difficult due to spectral overlap), Pb,  $\text{SO}_4$  (measured as S), Si, Sr, Ti, V, and Zn by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), for Sc, Cr, Mn, Co, Ni, Zn, Cu, Ga, Ge, Rb, Sr, Y, Mo, Cd, Cs, La, Ce, at CSIRO North Ryde Laboratories, and for Cs, Ba, Ga, Y, Mo, Ag, Sn, rare earth elements (REE), W, Hg, Tl, Bi, Th and U by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS) at the Mineral Science Laboratory, Chemistry Centre, WA. Total phosphate (as P) was measured in acidified waters by the molybdenum blue colorimetric method (Murphy and Riley, 1962). For Law1-16, I was determined by ICP-MS, whereas for Law17-20, I was determined by subtraction of P from P/I concentration.

One litre sub-samples of the filtered water were acidified with 1 mL 15 M  $\text{HNO}_3$  and one gram sachet of activated carbon and 25 - 30g of AR grade NaCl added. The bottles were rolled for eight days in the laboratory and the water discarded. The carbon was then analysed for Au by Neutron Activation (NAA). Laboratory investigations have indicated that this pre-concentration system permits successful analyses of waters for Au down to 0.005  $\mu\text{g/L}$  or lower. Calibration of the method was obtained by

shaking Au standards of varying concentrations, and in varying salinities, with activated carbon (Gray, unpublished data).

In addition, about 50 mL of the filtered water was collected separately, and analysed for Cl by the Technicon Industrial method (Zall *et al.*, 1956) at CSIRO Floreat Park Laboratories.

### 2.3 Speciation analysis

Speciation analysis involves computing parameters such as the solution species and degree of mineral saturation from the solution compositions, based on thermodynamic data. This is commonly done using the program PHREEQE (Parkhurst *et al.*, 1980; described in detail in Gray, 1990 and Gray, 1991), which determines the chemical speciation of many of the major and trace elements. To obtain highly accurate speciation data on a limited suite of the major elements (Na, K, Mg, Ca, Cl, HCO<sub>3</sub>, SO<sub>4</sub>, Sr and Ba), the specific ion interaction model known as the Pitzer equations was applied, using the program PHRQPITZ (courtesy USGS).

These programs are used to calculate the solubility indices (SI) for a number of mineral phases for each water sample. If the SI for a mineral equals zero (empirically from -0.2 to 0.2 for the major elements, and -1 to 1 for the minor elements which did not have Pitzer corrections), the water is in equilibrium with that particular solid phase, under the conditions specified. Where the SI is less than zero, the solution is under-saturated with respect to the phase, so that, if present, the phase may dissolve. If the SI is greater than zero the solution is over-saturated with respect to this phase and the phase can precipitate. Note that this analysis only specifies possible reactions, as kinetic constraints may rule out reactions that are thermodynamically allowed. Thus, for example, waters are commonly in equilibrium with calcite, but may become over-saturated with respect to dolomite, due to the slow rate of solution equilibration with this mineral (Drever, 1982).

The determinations are important in understanding solution processes at the site. They have particular value in determining whether the spatial distribution of an element is correlated with geological and/or mineralization phenomena or whether they are related to weathering or environmental effects. Thus, if Ca distribution is controlled by equilibrium with gypsum in all samples, then the spatial distribution of dissolved Ca will reflect SO<sub>4</sub> concentration alone and have no direct exploration significance.



### 3 RESULTS

#### 3.1 Compilation of results

Analytical results are compiled in Appendix 1. The total dissolved solids (TDS), a measure of groundwater salinity, were calculated from the major element contents. A number of the base metals were analysed using two or three techniques, with the "best" results (generally ICP-MS) given. On the basis of comparisons between methods (not included in this report), there were no significant discrepancies between analytical methods.

As discussed in Section 2.2, results from the Turrett pit are considered to be representative of the major ions only, and are therefore not used for most of the ensuing discussion.

#### 3.2 Comparison with results from other Yilgarn waters.

The groundwaters at Lawlers were neutral (pH range 6.5 - 8). An important comparison for these data is with other neutral groundwaters. Data for acid (pH < 6) groundwaters is not included as the solubility of many metals and pathfinder elements is enhanced in acid conditions, thus complicating any comparison between neutral and acid groundwaters. Averaged elemental data for the various groundwater groups are given in Table 2. Averaged data for all Lawlers samples are listed in Table 3, along with data for sea water (taken from Weast, 1983) and the averaged data for five other gold deposits with neutral groundwater (for Mt. Gibson and Mulgarrie, acid groundwaters samples were disregarded before averaging data):

- (i) Mt. Gibson: about 100 km north-east of Dalwallinu (central-west Yilgarn; Gray, 1991);
- (ii) Boags: a deposit at Bottle Creek, located 210 km north north-west of Kalgoorlie (central Yilgarn; Gray, 1992a);
- (iii) Golden Hope: a deposit at New Celebration some 40 km southeast of Kalgoorlie (south Yilgarn; Gray, 1993b);
- (iv) Granny Smith: about 25 km south of Laverton (central Yilgarn; Gray 1993a);
- (v) Mulgarrie: about 40 km north of Kalgoorlie (south Yilgarn; Gray 1992b).

Mt. Gibson, Boags and Golden Hope are designated as primarily residual sites. The Granny Smith groundwaters are divided into two groups: those from the north part of the study area (Goanna and Granny pits) which are primarily residual landforms; and samples from the southern part of the study area (Windich) which have appreciable overburden (Gray, 1993a). The Mulgarrie groundwaters are from a palaeodrainage covering a gold deposit.

Comparisons with other sites may be useful in indicating the degree of any particular element anomaly, and whether the groundwater composition is affected by particular lithological interactions.

The concentrations of various ions at Lawlers and at other sites are plotted *versus* TDS or *versus* pH in Appendix 2, Figures A2.1 - A2.44. The sea water data are used to derive the line of possible values if sea water were diluted with freshwater or concentrated by evaporation, hereafter denoted as the sea water line, and shown as the dotted line. Where the dotted line is not shown, this is because the sea water concentration is too low, relative to the concentration of the element in groundwaters, to be observed on the graph.

The salinity of the Lawlers groundwaters are appreciably less than that of the other sites studied, so that when a scale where most of the Lawlers data can be resolved is used, only some of the groundwaters from the previous sites are observed.

Table 2: Averaged compositions of the Lawlers groundwater groups.

	Fairyland (3) #		Genesis (3)		Gt. Eastern / Caroline (6)		Hidden Secret (3)		Waroonga (9)		Four Corners - south (4)		Four Corners - north (11)	
	mean	std dv @	mean	std dv	mean	std dv	mean	std dv	mean	std dv	mean	std dv	mean	std dv
pH	7.7	0.2	7.4	0.2	7.0	0.2	6.9	0.1	7.0	0.2	7.4	0.1	7.4	0.1
Eh (mV)	220	70	250	120	250	20	280	30	290	50	230	40	290	20
Na *	0.23	0.00	0.23	0.01	0.18	0.05	0.26	0.07	0.20	0.01	0.24	0.04	0.21	0.02
Mg *	0.135	0.007	0.069	0.002	0.102	0.020	0.057	0.022	0.061	0.005	0.055	0.015	0.048	0.005
Ca *	0.018	0.001	0.081	0.005	0.113	0.036	0.035	0.028	0.083	0.006	0.038	0.021	0.079	0.016
K *	0.015	0.001	0.021	0.002	0.013	0.008	0.011	0.001	0.024	0.006	0.019	0.004	0.025	0.003
Cl *	0.26	0.02	0.33	0.02	0.22	0.07	0.39	0.08	0.31	0.04	0.34	0.07	0.29	0.01
SO <sub>4</sub> *	0.11	0.01	0.15	0.00	0.12	0.07	0.23	0.08	0.17	0.02	0.22	0.02	0.23	0.02
HCO <sub>3</sub>	240	60	64	4	170	50	50	30	80	20	170	40	116	10
TDS	530	50	510	60	500	190	3000	1300	460	150	1240	270	710	80
Li	nd	-	nd	-	nd	-	nd	-	<0.005	-	<0.005	-	<0.005	-
Rb	0.009	0.000	0.008	0.002	0.003	0.002	0.016	0.006	0.009	0.003	0.012	0.002	0.010	0.004
Sr	0.20	0.01	0.29	0.04	0.25	0.10	0.9	0.7	0.26	0.10	0.52	0.11	0.40	0.08
Cs	0.0004	0.0000	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-
Ba	0.011	0.002	0.046	0.006	0.10	0.08	0.062	0.028	0.048	0.016	0.026	0.002	0.029	0.012
B	nd	-	nd	-	nd	-	nd	-	0.48	0.13	2.0	0.5	0.86	0.11
Al	<0.002	-	0.003	0.002	0.008	0.007	0.002	0.001	0.002	0.001	0.006	0.006	0.007	0.010
Si	7	0	29	1	27	8	23	7	29	7	16	4	24	7
P	0.03	0.03	0.06	0.06	0.04	0.02	0.32	0.10	0.09	0.07	0.004	0.004	0.011	0.014
I	0.3	0.1	0.3	0.1	0.1	0.1	1.2	0.9	0.3	0.1	0.2	0.5	0.5	0.1
Sc	0.006	0.001	0.024	0.001	0.023	0.007	0.018	0.006	0.005	0.004	<0.001	-	0.003	0.004
Ti	<0.002	-	<0.002	-	<0.002	-	<0.002	-	<0.002	-	<0.002	-	<0.002	-
V	nd	-	nd	-	nd	-	nd	-	0.017	0.014	0.007	0.003	0.008	0.006
Cr	0.27	0.07	0.014	0.004	0.001	0.001	0.006	0.003	0.005	0.006	0.039	0.054	0.007	0.008
Mn	0.007	0.004	0.004	0.006	0.22	0.25	0.14	0.08	0.02	0.03	0.03	0.05	0.02	0.05
Fe	0.012	0.010	0.007	0.005	0.013	0.011	0.039	0.019	0.003	0.000	0.005	0.002	0.004	0.004
Co	0.000	0.001	0.001	0.002	0.07	0.17	0.15	0.11	0.001	0.001	0.000	0.001	0.001	0.002
Ni	0.007	0.002	0.005	0.002	0.009	0.004	0.029	0.017	0.003	0.002	0.002	0.001	0.004	0.005
Cu	0.005	0.004	0.002	0.001	0.004	0.003	0.008	0.003	0.001	0.003	0.000	0.001	0.000	0.001
Zn	0.009	0.015	0.007	0.009	0.018	0.015	0.020	0.016	0.007	0.005	0.005	0.001	0.006	0.003
Ga	0.0005	0.0001	0.0019	0.0003	0.0039	0.0032	0.0029	0.0012	0.0017	0.0005	0.0010	0.0001	0.0014	0.0010
Ge	0.0005	0.0004	<0.0005	-	<0.0005	-	0.0011	0.0003	<0.0005	-	<0.0005	-	<0.0005	-
As	0.004	0.001	0.11	0.03	0.006	0.003	0.08	0.09	nd	-	nd	-	nd	-
Y	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-
Zr	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-
Mo	<0.001	-	0.001	0.000	0.007	0.004	0.003	0.002	0.001	0.001	0.002	0.000	0.003	0.002
Ag	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-	<0.001	-
Cd	<0.002	-	<0.002	-	<0.002	-	<0.002	-	<0.002	-	<0.002	-	<0.002	-
Sn	0.0002	0.0002	<0.0001	-	0.0001	0.0001	<0.0001	-	nd	-	nd	-	nd	-
Sb	<0.0001	-	0.0003	0.0002	<0.0002	-	0.0028	0.0019	<0.0002	-	<0.0002	-	<0.0002	-
La	0.0003	0.0003	<0.0002	-	<0.0002	-	0.0008	0.0006	<0.0002	-	<0.0002	-	<0.0002	-
Ce	<0.0002	-	<0.0002	-	<0.0002	-	0.0007	0.0005	<0.0002	-	<0.0002	-	<0.0002	-
Pr	<0.0002	-	<0.0002	-	<0.0002	-	0.0003	0.0003	<0.0002	-	<0.0002	-	<0.0002	-
Nd	<0.0002	-	<0.0002	-	<0.0002	-	0.0007	0.0007	<0.0002	-	<0.0002	-	<0.0002	-
Sm	<0.0002	-	<0.0002	-	<0.0002	-	0.0003	0.0003	<0.0002	-	<0.0002	-	<0.0002	-
Eu	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-
Gd	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-
Tb	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-
Dy	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-
Ho	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-
Er	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-
Tm	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-
Yb	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-
Lu	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	nd	-	nd	-	nd	-
W	<0.0005	-	<0.0005	-	0.0006	0.0005	0.008	0.014	<0.0005	-	<0.0005	-	<0.0005	-
Au	0.008	0.006	2	3	4	9	28	13	0.010	0.007	0.022	0.004	0.008	0.007
Hg	0.0009	0.0009	<0.0002	-	0.0003	0.0006	0.0004	0.0005	<0.0002	-	<0.0002	-	<0.0002	-
Tl	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-	<0.0002	-
Pb	0.002	0.001	0.001	0.000	0.002	0.001	0.001	0.000	0.001	0.000	0.001	0.000	0.001	0.000
Bi	<0.0003	-	<0.0003	-	<0.0003	-	<0.0003	-	<0.0003	-	<0.0003	-	<0.0003	-
Th	<0.0005	-	<0.0005	-	<0.0005	-	<0.0005	-	<0.0005	-	<0.0005	-	<0.0005	-
U	0.0003	0.0001	0.0007	0.0001	0.0024	0.0016	0.005	0.007	0.0005	0.0002	0.0014	0.0002	0.0006	0.0002

Table 3: Averaged compositions of Lawlers groundwaters, with averaged results from other sites and sea water given for comparison.

	Lawlers (40) #		Mt Gibson (39)	Boags (2)	Golden Hope (3)	Granny Smith - Residual (7)	Granny Smith - Covered (11)	Mulgarrie (6)	Sea Water
	mean	std dv @							
pH	7.26	0.35	6.41	6.61	6.35	7.38	7.25	6.83	
Eh (mV)	270	50	330	160	200	270	240	180	
Na *	0.21	0.04	0.33	0.25	0.27	0.32	0.33	0.29	0.30
Mg *	0.070	0.029	0.031	0.052	0.062	0.026	0.023	0.052	0.039
Ca *	0.07	0.03	0.01	0.03	0.01	0.02	0.03	0.01	0.01
K *	0.020	0.007	0.011	0.009	0.006	0.010	0.010	0.004	0.011
Cl *	0.30	0.06	0.54	0.47	0.52	0.47	0.46	0.54	0.55
SO <sub>4</sub> *	0.18	0.06	0.08	0.17	0.13	0.14	0.12	0.10	0.08
HCO <sub>3</sub>	120	60	220	620	690	210	170	400	140
TDS	800	800	19000	21000	45000	21000	7000	41900	34400
Li	<0.005	-	0.08	nd	nd	nd	nd	nd	0.18
Rb	0.009	0.004	nd	nd	nd	nd	nd	nd	0.12
Sr	0.37	0.25	2.0	5.9	6.7	2.3	1.4	8.4	8.1
Cs	<0.0002	-	nd	nd	0.05	0.005	0.002	nd	0.0005
Ba	0.05	0.04	0.04	0.01	0.04	0.03	0.03	0.05	0.03
B	0.9	0.6	nd	nd	nd	nd	nd	nd	4.6
Al	0.005	0.007	0.03	<0.01	0.04	0.005	0.011	0.04	0.01
Si	24	8	29	7.2	8	8.5	22	12	3
P	0.04	0.06	nd	nd	0.05	0.01	0.02	nd	0.06
I	0.5	0.4	0.4 <sup>S</sup>	2.1 <sup>S</sup>	2.8 <sup>S</sup>	1.3	0.6	0.5 <sup>S</sup>	0.06
Sc	0.010	0.010	nd	nd	nd	nd	nd	nd	nd
Ti	<0.002	-	nd	nd	nd	<0.002	<0.002	nd	0.001
V	0.011	0.010	nd	nd	nd	nd	nd	nd	0.002
Cr	0.03	0.08	<0.02	0.002	0.002	<0.005	<0.005	0.03	0.00005
Mn	0.06	0.12	0.6	0.03	0.32	0.6	0.19	4	0.002
Fe	0.008	0.012	3	0.07	3	0.2	0.5	0.04	0.01
Co	0.02	0.08	<0.05	<0.005	0.004	0.03	0.005	0.06	0.00027
Ni	0.007	0.008	<0.1	<0.01	0.03	0.06	0.013	0.14	0.005
Cu	0.002	0.003	<0.03	0.008	0.040	0.003	0.03	0.021	0.003
Zn	0.009	0.010	<0.2	0.015	0.014	0.10	0.05	0.03	0.01
Ga	0.002	0.002	nd	nd	0.009	0.001	0.001	nd	0.00003
Ge	<0.0005	-	nd	nd	nd	nd	nd	nd	0.00007
As	0.04	0.06	nd	0.11	<0.02	0.06	0.03	<0.02	0.003
Y	<0.0002	-	nd	nd	0.004	<0.0001	0.0002	nd	0.0003
Zr	<0.001	-	nd	nd	nd	nd	nd	nd	0.00002
Mo	0.003	0.003	nd	nd	0.019	0.03	0.025	nd	0.01
Ag	<0.001	-	nd	nd	0.0041	0.0003	0.0001	nd	0.0003
Cd	<0.002	-	nd	0.009	0.001	0.002	<0.002	nd	0.00011
Sn	0.0001	0.0001	nd	nd	0.003	0.001	0.0005	nd	0.003
Sb	0.0003	0.0008	nd	0.17	<0.0003	0.007	0.002	<0.0003	0.0003
La	<0.0002	-	nd	nd	0.0010	0.0001	0.0003	nd	0.000004
Ce	<0.0002	-	nd	nd	0.0013	0.0001	0.0013	nd	0.0000008
Pr	<0.0002	-	nd	nd	0.0002	<0.0001	0.0002	nd	nd
Nd	<0.0002	-	nd	nd	0.0007	0.0001	0.0006	nd	0.000002
Sm	<0.0002	-	nd	nd	0.0003	0.0001	0.0002	nd	0.0000005
Eu	<0.0002	-	nd	nd	0.0001	<0.0001	0.0001	nd	0.0000001
Gd	<0.0002	-	nd	nd	0.0003	0.0001	0.0002	nd	0.0000007
Tb	<0.0002	-	nd	nd	<0.0001	0.0001	0.0001	nd	nd
Dy	<0.0002	-	nd	nd	0.0002	0.0001	0.0001	nd	0.0000009
Ho	<0.0002	-	nd	nd	<0.0001	0.0001	0.0001	nd	nd
Er	<0.0002	-	nd	nd	0.0002	<0.0001	<0.0001	nd	0.0000008
Tm	<0.0002	-	nd	nd	<0.0001	<0.0001	<0.0001	nd	nd
Yb	<0.0002	-	nd	nd	0.0002	<0.0001	<0.0001	nd	0.0000008
Lu	<0.0002	-	nd	nd	<0.0001	<0.0001	<0.0001	nd	0.0000002
W	0.001	0.004	nd	nd	0.056	<0.0001	0.001	nd	0.0001
Au	3	9	0.16	0.5	0.004	0.03	0.006	0.05	0.011
Hg	<0.0002	-	nd	nd	0.0039	0.0002	0.0004	nd	0.00003
Tl	<0.0002	-	nd	nd	0.0006	0.0003	<0.0002	nd	0.000005
Pb	0.001	0.001	0.11	0.008	0.03	0.019	0.003	0.007	0.00005
Bi	<0.0003	-	nd	<0.002	<0.0001	<0.0003	<0.0003	<0.002	0.00002
Th	<0.0005	-	nd	nd	<0.0005	<0.0005	<0.0005	nd	0.00005
U	0.001	0.002	nd	<0.002	0.010	0.004	0.012	<0.002	0.003

Abbreviations for Tables 2 and 3:

All concentrations in mg/L, except Au in  $\mu\text{g/L}$ .

Eh is measured in mV.

# Bracketed numbers denote the number of samples.

@ Standard Deviation or detection limit (whichever is the larger).

\* For the elements Na, Mg, Ca, K, Cl and  $\text{SO}_4$ , the ratio of the element concentration to TDS is used rather than the concentration. (See Section 3.4 for details.)

\$ Free iodide ( $\text{I}^-$ ) rather than total I

nd not determined                      - not applicable



### 3.3 Acidity and oxidation potential

An Eh-pH plot of waters from Lawlers and other sites (including acid groundwater sites Panglo, Yalanbee and Wollubar; Gray, 1990, 1993b) is shown in Figure 5. The Lawlers groundwaters are neutral ( $6.5 < \text{pH} < 8$ ) and have a similar Eh range to neutral waters from other sites.

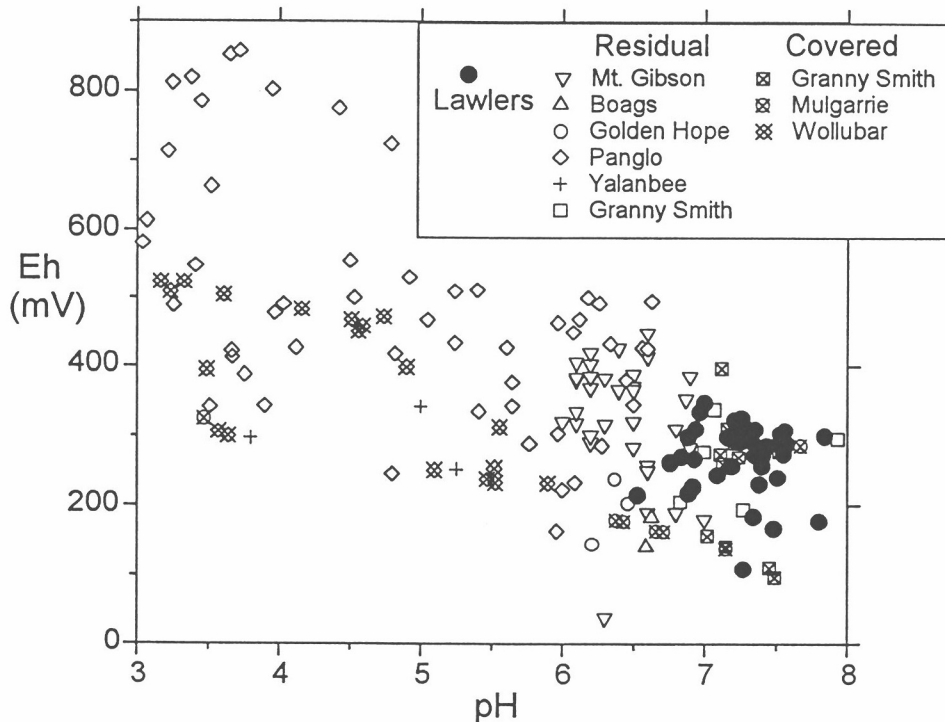
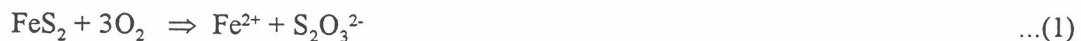


Figure 5: Eh vs. pH for groundwaters from Lawlers and other sites.

The neutral pH of the water samples indicate that any sulphide present will be oxidizing under neutral conditions. Under such a regime, significant concentrations of the intermediate sulphur compounds thiosulphate ( $\text{S}_2\text{O}_3^{2-}$ ) and sulphite ( $\text{SO}_3^{2-}$ ) are commonly produced (Granger and Warren, 1969; Goldhaber, 1983; Webster, 1984):



This may have consequences for the groundwater mobility of Au, as discussed in Section 3.6.

### 3.4 Major ion chemistry

For the ions Na, Mg, Ca, K, Cl and  $\text{SO}_4$ , the ratio of the concentration divided by TDS (hereafter called the TDS ratio) is used in Tables 2 and 3 rather than the concentration. This is because the chemistries of these ions are primarily controlled by salinization effects and therefore better understood by using the TDS ratio. Additional information may also be obtained from concentration vs. TDS plots (Figures A2.1 - A2.12). The TDS ratios for most of the major elements diverge markedly from that of sea water. In particular, the major ions Na and Cl are highly depleted, relative to sea water, whereas the other ions are proportionally enriched at Lawlers. The divergences are sufficiently great to suggest that Lawlers (unlike other sites previously studied) does not represent groundwater that is predominantly derived from sea water (albeit with minor depletions or enrichments), but is instead a groundwater for which the major ion abundances are strongly controlled by local lithological or hydrological factors.

The potential for dissolution or precipitation of minerals such as gypsum from the Lawlers groundwaters is tested by speciation analysis (Section 2.3). The range, average and standard deviation of the SI values of the water samples for a number of relevant solid phases are given in Table 4, with SI values plotted in Appendix 3. As discussed in detail in Section 2.3, a SI of zero indicates the solution is saturated with respect to that mineral, a SI less than zero indicates under-saturation and a SI greater than zero indicates the solution is over-saturated with respect to the mineral phase.

Table 4: SI Values for the Lawlers groundwaters, for a number of relevant solid phases.

Mineral	Formula	Lower	Upper	Mean	Standard Deviation
Halite	NaCl	-7.3	-4.3	-6.2	0.6
Gypsum	CaSO <sub>4</sub> .2H <sub>2</sub> O	-4.0	-0.7	-1.9	0.5
Celestine	SrSO <sub>4</sub>	-4.7	-1.2	-2.4	0.6
Barite	BaSO <sub>4</sub>	-2.1	0.6	-0.4	0.5
Calcite	CaCO <sub>3</sub>	-2.0	-0.3	-0.8	0.4
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	-3.7	0.6	-1.0	0.9
Magnesite	MgCO <sub>3</sub>	-2.5	0.1	-1.1	0.5
Quartz	SiO <sub>2</sub>	0.4	1.1	0.9	0.2
Amorphous Silica	"	-0.9	-0.1	-0.4	0.2
Gibbsite	Al(OH) <sub>3</sub>	-0.1	1.2	0.6	0.4
Amorphous Alumina	"	-2.4	-1.0	-1.7	0.4
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	1.9	5.3	3.8	0.9
Siderite	FeCO <sub>3</sub>	-4.7	-1.7	-2.7	0.9
Ferrihydrite	Fe <sub>2</sub> O <sub>3</sub> .nH <sub>2</sub> O	0.9	2.0	1.5	0.3
Goethite	FeOOH	5.8	7.0	6.5	0.3
Rhodochrosite	MnCO <sub>3</sub>	-2.8	0.2	-1.8	0.8
Tenorite	Cu(OH) <sub>2</sub> .H <sub>2</sub> O	-2.8	-0.7	-1.7	0.5
Smithsonite	ZnCO <sub>3</sub>	-4.3	-2.0	-3.3	0.4
Cerussite	PbCO <sub>3</sub>	-2.4	-0.7	-1.7	0.3
Theophrasite	Ni(OH) <sub>2</sub>	-5.0	-2.3	-3.7	0.6
Sphaerocobaltite	CoCO <sub>3</sub>	-4.9	-1.6	-4.0	0.8
Eskolaite	Cr <sub>2</sub> O <sub>3</sub>	3.2	11.4	6.6	2.0
Au Metal	Au	3.8	9.5	5.7	1.6
Sb(OH) <sub>3</sub>	Sb(OH) <sub>3</sub>	-1.4	-0.3	-0.9	0.4
Pb <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	Pb <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	-0.7	0.3	-0.4	0.3
Carnotite	K <sub>2</sub> (UO <sub>2</sub> ) <sub>2</sub> (VO <sub>4</sub> ) <sub>2</sub> .3H <sub>2</sub> O	-3.3	-2.3	-2.8	0.3

Groundwaters at Lawlers are undersaturated with respect to halite, gypsum and celestine (Figures A3.1 - A3.3), in contrast with the majority of sites in the south Yilgarn in which waters are saline to hypersaline and saturated with these salts. However, similarly to other sites, Lawlers groundwaters reach barite saturation (Figure A3.4). Note that a groundwater sampled at Hidden Secret, which has the highest Au concentration (up to 41 µg/L), is significantly oversaturated with respect to barite, possibly because Ba is being released by weathering reactions (such as carbonate dissolution) faster than it can equilibrate with barite. Lawlers groundwaters are undersaturated to saturated with respect to calcite, dolomite and magnesite (Figures A3.5 to A3.7), as previously observed at the other, more

saline, sites. At those sites, the great excess of Mg and Ca relative to bicarbonate means that carbonate equilibration will control bicarbonate concentrations but have little direct effect on those of Mg and Ca. In contrast, the Lawlers groundwaters are fresher and Mg and Ca concentrations approximately match that of bicarbonate, so that equilibration with carbonate minerals will therefore have a strong effect on the Mg and Ca concentration. This is presumably reflected in the major deviation from linearity for Mg and Ca, relative to sea water (Figures A2.3 and A2.4).

The upper limit for  $\text{HCO}_3^-$  concentration is less than at other sites (Figure A2.12), with some groundwaters having particularly low  $\text{HCO}_3^-$  contents. This is particularly marked for the Au-rich Hidden Secret samples and is similar to neutral Au-rich groundwater from the Hornet ore body, Mt. Gibson (Gray, 1991), which also had a very low  $\text{HCO}_3^-$  concentration.

Aluminium concentrations are low in the Lawlers groundwaters, approximating that of sea water (Figure A2.17), again consistent with the neutral pH. All waters are saturated or oversaturated with respect to gibbsite, but are undersaturated with respect to amorphous alumina (Figure A3.9). Similarly, the groundwaters are oversaturated with respect to quartz but undersaturated with respect to amorphous silica (Figure A3.8), perhaps reflecting the presence of phases such as opaline silica. Dissolved Si concentrations are above that for sea water but approximately match other sites (Figure A2.18).

Dissolved Fe concentrations (Figure A2.23) are very low. The groundwaters are undersaturated with respect to siderite ( $\text{FeCO}_3$ ; Figure A3.11), a  $\text{Fe}^{\text{II}}$  carbonate, and moderately oversaturated with respect to ferrihydrite (Figure A3.12), a highly soluble  $\text{Fe}^{\text{III}}$  oxide. Manganese concentrations are similar to other sites (Figure A2.22) and some groundwaters are saturated with respect to rhodochrosite ( $\text{MnCO}_3$ ; Figure A3.13).

### 3.5 Minor element chemistry

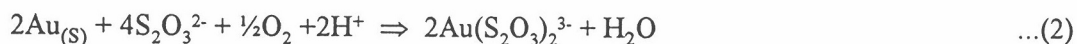
Most of the minor elements have concentrations similar to those at other sites (Table 2; Figures A2.21 - A2.44). As discussed previously, Fe concentrations are significantly lower at Lawlers than elsewhere. Chromium is high at Lawlers and Mulgarrie, due to the presence of ultramafic rocks. However, Ni concentrations are low at Lawlers, consistent with observations at Panglo (Gray, 1990) suggesting that Cr is quickly dissolved during neutral weathering of ultramafic rocks, whereas most of the Ni is included in more resistant minerals and will only be released during acid weathering.

Most minor elements are undersaturated with respect to the least soluble mineral phase (Table 4; also see Figures A3.14 - A3.23), indicating little dissolution of these elements and/or removal from solution via mechanisms such as sorption. Exceptions are Sb, Pb, V and Cr, with groundwaters reaching equilibrium with respect to solid  $\text{Sb}(\text{OH})_3$  (Figure A3.21) and  $\text{Pb}_2\text{V}_2\text{O}_7$  (Figure A3.22) and being strongly oversaturated with respect to eskolaite ( $\text{Cr}_2\text{O}_3$ ; Figure A3.19). This is consistent with above suggestions that Cr is being released from weathering minerals, and with groundwaters not equilibrating with less soluble Cr minerals.

### 3.6 Gold chemistry

Some of the groundwaters at Lawlers have extremely high concentrations of dissolved Au (Figure A2.40): the highest observed concentration of 40  $\mu\text{g/L}$  is 10 times greater than any other reported groundwater Au concentration (see papers listed in Gray, 1988, Section 1). The observed Au anomalies are highly localized in deeper groundwaters within mineralized zones. On the basis of previous work (Gray, 1988 and references given therein), the most likely form of dissolved Au at Lawlers is as the thiosulphate complex  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ . The thiosulphate ion is commonly released during weathering of sulphide minerals under neutral conditions (Eqn. 1), which appear to match

conditions at Lawlers (Section 3.3). Once formed, thiosulphate will readily dissolve Au (Lakin *et al.*, 1974; Mann and Webster, 1990):



The reason for the very high Au concentration in groundwaters at Lawlers is not clear. The high Au samples at Hidden Secret and Gt. Eastern/Caroline all have highly anomalous Co concentrations (Figure A2.24). The Co anomaly is even more clearly observed when Co concentration is plotted vs. Mn (Figure A2.27) compared with the generally good correlation of other transition metals such as Ni with Mn (Figure A2.28). Cobalt is commonly correlated with Mn in groundwater (Gray, 1993b), with Co concentration in most samples about  $\frac{1}{20}$  that of Mn: therefore groundwaters with anomalous Co concentrations can be identified by calculating the Co excess (=  $\text{Co} - \text{Mn}/20$ ). When Au concentration is plotted vs. Co excess (Figure 6), there is a clear correlation between anomalous Au and anomalous Co, notably for the Hidden Secret and Gt. Eastern/Caroline groundwaters. This effect may be related to Co enrichment in the original ore.

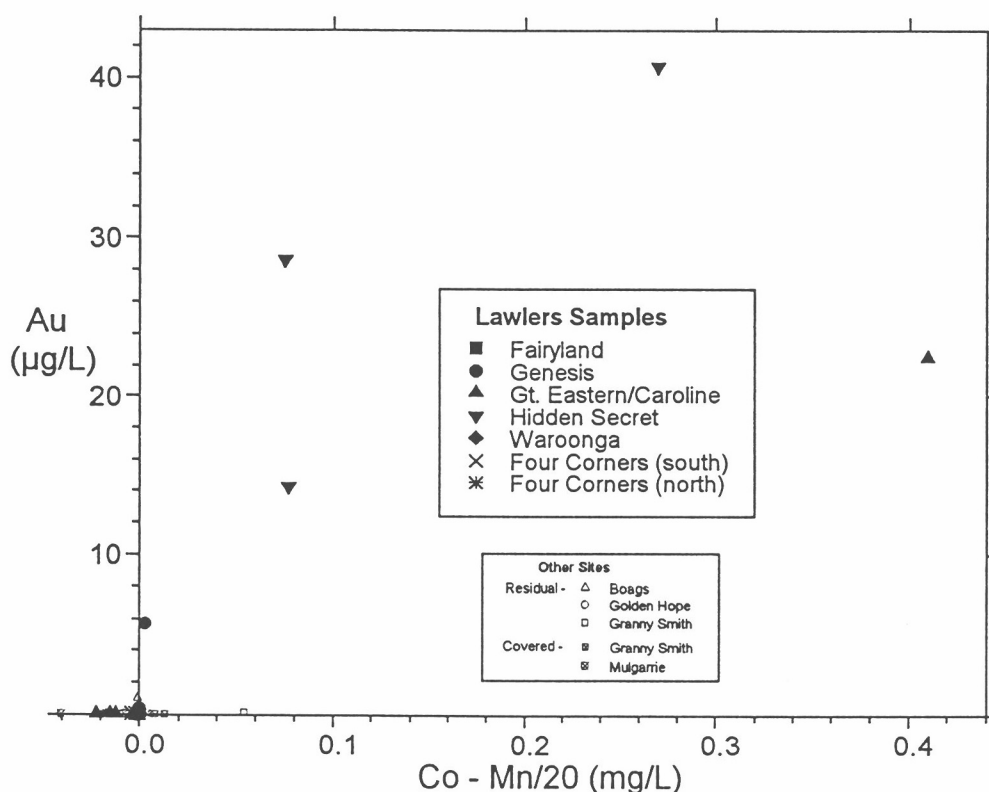


Figure 6: Au concentration vs Co excess ( $\text{Co} - \text{Mn}/20$ ) for groundwaters from Lawlers and other sites.

The Genesis groundwater sample with a high dissolved Au concentration differed from the other high Au groundwaters in that the Co anomaly factor was low (Figure 6). This difference between groundwater at Genesis and at the other ore bodies is discussed further in Section 4.2.

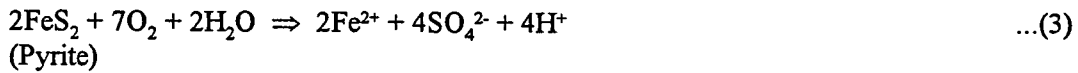


## 4 COMPARISONS BETWEEN GROUNDWATER GROUPS

The varying groundwater groups distinguished at Lawlers are listed in Section 2.2. Each of these groups had distinctive groundwater chemistry, as is detailed below.

### 4.1 Major ions

At other sites investigated in the Yilgarn Block, groundwaters are generally saline, with the highest salinities observed in the lowlands, and the lowest salinities in recharge areas. Under these conditions, exploration methods using the halide ions Cl and Br (see Frick *et al.*, 1989 and references given therein) will be of little use due to high background concentrations, though dissolved I concentrations appear to have exploration potential (Gray, 1990, 1991, 1992a,b, 1993b). In contrast, it appears that at Lawlers, due to the low salinity, many of the major ion concentrations, as well as I, are controlled by lithological effects. Thus, Hidden Secret groundwaters are more saline than elsewhere, despite the area being closer to the groundwater divide than Genesis or Waroonga. In particular, at Hidden Secret the waters most enriched in Au are also relatively enriched in Mg, Ca, SO<sub>4</sub> and HCO<sub>3</sub> (Figure 7). The SO<sub>4</sub> is possibly released from the oxidation of pyrite and other sulphide minerals:



with Mg, Ca and HCO<sub>3</sub> released from carbonate dissolution by acid produced by sulphide oxidation:

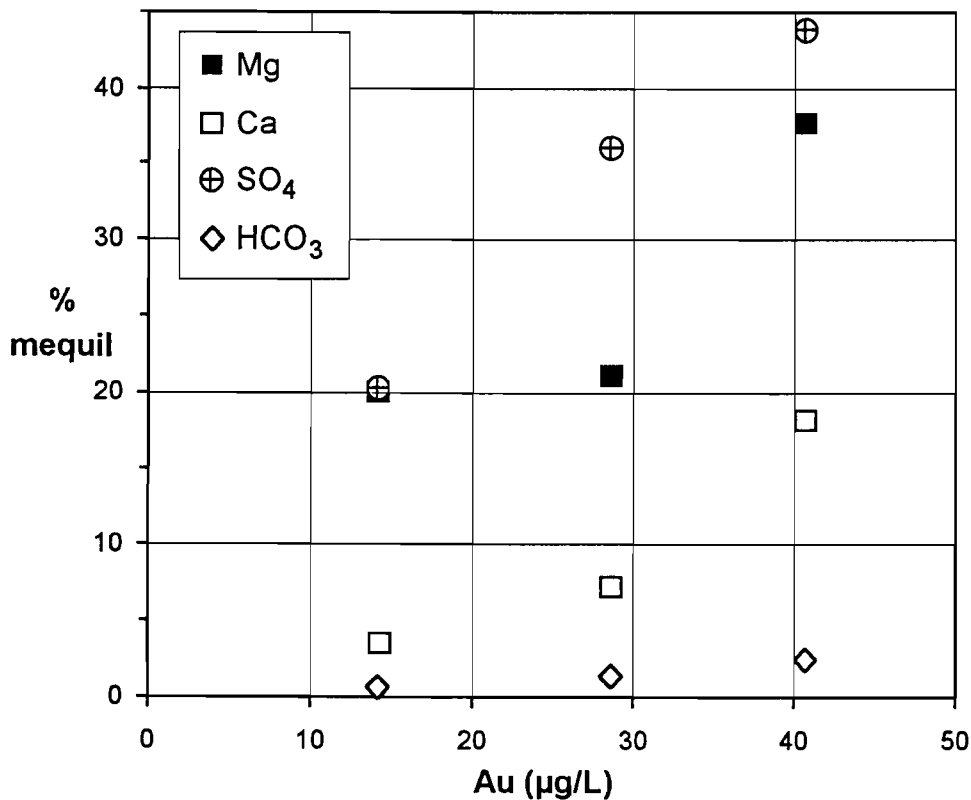
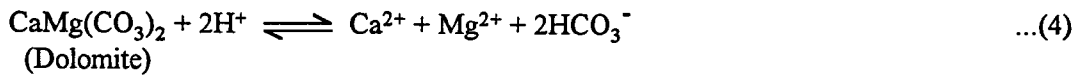


Figure 7: Proportional Mg, Ca, SO<sub>4</sub> and HCO<sub>3</sub> concentrations vs. Au for Hidden Secret groundwaters.

Groundwaters in the southern section of Four Corners are distinctly more saline (860 - 1400 mg/L TDS) than to the north (550 - 790 mg/L TDS), despite surface water flow being northward. Possible reasons for this are discussed in Section 5.2.

The other groundwaters from the Lawlers area have low salinities, with TDS between 300 and 790 mg/L (Table 2).

## 4.2 Gold

Anomalously high Au concentrations occur in groundwaters from Hidden Secret and Genesis, and at the site closest to the Gt. Eastern and Caroline pits. As discussed in Section 3.6, it is expected that the Au is complexed by the thiosulphate ion ( $S_2O_3^{2-}$ ). Conditions at these sites would appear to be highly favourable to the generation of this complex, though at present it is not clear why these sites should be different from others previously investigated. The Four Corners area, though with a significant Au resource, has a poor Au groundwater response (Figure A2.40)

## 4.3 Minor ions

There are differences in the minor element distribution for the various groundwater groups, which in many instances may be related to lithology or mineralization:

- (i) Fairyland groundwaters are low in Ca and enriched in Cs and Cr - presumably because these groundwaters are from an ultramafic aquifer;
- (ii) Genesis groundwaters are enriched in Sc and As, possibly due to mineralization;
- (iii) Groundwaters from the Gt. Eastern/Caroline area are enriched in Ba, Sc, Mo and to a lesser extent Al, Mn, Ga and U;
- (iv) Hidden Secret groundwaters are highly enriched in P, Co, Ni, Ge, As, Y and REE, Sb and W and have moderate enrichments in Sc, I and U - these groundwaters are also highly anomalous in Au;
- (v) there are no significant minor element anomalies for the Waroonga and Four Corners (south and north) groundwater groups, though interestingly the three groups could be distinguished by B (Figure A2.14) and, to a lesser degree, I concentration (Figure A2.15).

The three groundwater groups in areas of major Au mineralization (Genesis, Gt. Eastern/Caroline, Hidden Secret) all have significant minor element anomalies. The differences in the minor element 'signature' may reflect differences in the lithologies of the three sites and/or the geochemistry of the Au mineralization. Neutral groundwaters contacting mineralized rocks at Gt. Eastern/Caroline and Hidden Secret resemble those at other sites in the Yilgarn (Mt. Gibson, Boags, Mulgarrie, Golden Hope) with anomalies in a range of chalcophile and other pathfinder elements. In contrast, the Genesis groundwaters have a particularly limited (and distinctive) 'signature', being patchily anomalous in Au (Section 4.3), and with relatively uniform Sc and As. The Genesis ore deposit differs from other sites, consisting of thin, mineralized quartz veins hosted by quartzite. Although arsenopyrite is disseminated throughout the ore body (presumably causing the groundwater As anomaly), Au is only rarely associated with it.

## 5 MAPPING OF THE DATA

### 5.1 Description of the mapping

Element distributions determined by groundwater sampling are given in Appendix 4, as pairs of maps on facing pages. The entire area is shown on the left page, with the Hidden Secret/Genesis/Waroonga and Four Corners areas enlarged to facilitate interpretation. The hatched area in the Four Corners insert is the area of mineralization. The right page has a map of the Four Corners area alone. The geology of the study area is given in Figure A4.1 and outlines of the principal units are shown on the distribution maps. The Au distribution in the bedrock at Four corners is shown in Figure A4.2 and repeated on the detailed maps.

### 5.2 Total dissolved solids and salinity-related elements

*Total dissolved solids* (Figures A4.3 and A4.4): The salinities of the samples vary from 200 to 4300 mg/L TDS. Greatest salinities are observed at Hidden Secret, possibly related to mineralization (Section 4.1). High salinities are also observed in the southern part of Four Corners, contrary to the generally expected groundwater flow from south to north in this area. This could be due to:

- (i) groundwater flow being opposite to surface flow;
- (ii) a separate, more saline, aquifer in the south part of Four Corners, recharged through the shear in the south west of the area (Figure A4.1);
- (iii) higher salinities being correlated with the strike of the mineralization.

The final hypothesis is of most interest from an exploration viewpoint but the highest salinities are south of the mineralization. Hypothesis (ii) is considered most likely, though there is no definitive proof at this time. Nor, indeed, are the hypotheses mutually exclusive.

Data for the major ions Na, K, Mg, Ca, Cl, SO<sub>4</sub> and Br are shown in Figures A4.5 - A4.17 as the ratio over TDS. The total ion concentrations would give very similar distributions to TDS, whereas the ratio may give critical information on the enrichment in groundwater of a particular ion (see Section 3.4).

*Sodium, potassium, magnesium, calcium and chlorine* (Figures A4.5 - A4.14): These ions show few clear patterns and have distributions similar to TDS. The southern part of the Four Corners area is depleted in K, and possibly enriched in Na and Cl, relative to the northern part (Figures A4.6, A4.8 and A4.14).

*Sulphate* (Figures A4.15 and A4.16): Sulphate enrichment in mineralized areas has been observed at Boags and Golden Hope (Gray, 1992a, 1993b). Similar enrichment is present in Au-rich groundwaters at Hidden Secret and Gt. Eastern/Caroline. Groundwaters at Four Corners are relatively SO<sub>4</sub>-rich (Figure A4.16), and the area of Au mineralization has a greater SO<sub>4</sub> ratio than groundwaters in the surrounding barren area. Therefore, with the exception of the Genesis deposit, the SO<sub>4</sub>/TDS ratio appears to effectively indicate mineralization in the Lawlers study area.

*Bromine* (Figure A4.17): Based on limited data, the range in the Br/TDS ratio is much less than for the other major ions, indicating a close relationship between Br and salinity. There is a possible Br enrichment for single groundwater samples at Hidden Secret and Genesis.

*Rubidium and caesium* (Figures A4.18 - A4.20): Rubidium and Cs distributions are variable, possibly because measured values are low. Caesium concentrations do appear to be enhanced in groundwaters contacting ultramafic rocks.

*Strontium* (Figures A4.21 and A4.22): Strontium and Ca are generally highly correlated in groundwater (Gray, 1993b) and the Sr/Ca ratio is therefore plotted rather than Sr. Strontium is enriched in the Fairyland groundwaters. At Four Corners (Figure A4.22), Sr is enriched in the south of the study area, indicating (as do TDS and K) differing groundwater conditions in this part of the study area.

*Barium* (Figures A4.23 and A4.24): Though an alkaline earth metal, Ba commonly shows differing behaviour from Sr and Ca, partially because of a major solubility control by equilibration with barite, and possibly because Ba is associated with mineralization. The enrichment of Ba in Hidden Secret groundwaters has significance, with one sample significantly oversaturated with respect to barite (Section 3.4). This may be due to dissolved Ba being released by weathering reactions (such as carbonate dissolution) faster than it can precipitate as barite. Barium distribution at Four Corners is highly variable, although, interestingly, the groundwater sampled in the centre of the mineralized area had the highest level of barite saturation in the area.

*Boron* (Figures A4.25 and A4.26): Boron concentrations, like TDS, K and Sr, distinguish the southern and northern groundwater systems at Four Corners.

*Phosphorus* (Figures A4.27 and A4.28): Phosphorus concentrations are highest at Hidden Secret, matching results for a number of elements. In general, concentration appear greater in the Hidden Secret/Genesis/Waroonga area, perhaps reflecting higher concentrations in groundwater from the sandstone aquifer in this area (Figure 3). There is a possible minor P enhancement in groundwater adjacent to mineralization in the Gt. Eastern/Caroline area.

### 5.3 Acidity, alkalinity and oxidational potential

*Acidity* (Figure A4.29 and A4.30): The pH distribution is narrow (6.5 - 8.5), with waters associated with ultramafic rocks (Fairyland, Turrett) having the highest pH values.

*Bicarbonate* (Figure A4.31 and A4.32): Greatest  $\text{HCO}_3$  concentrations are observed at Fairyland and in the southern part of the Gt. Eastern/Caroline area. Concentrations are higher in the southern part of Four Corners than to the north (Figure A4.32), similar to various salinity-related ions (Section 5.2).

*Oxidation potential* (Figure A4.33 and A4.34): The highest Eh values are observed in the Waroonga and Genesis groundwaters, perhaps reflecting the different lithology (sandstones and other sediments) in the western part of the study area.

### 5.4 Aluminium, gallium and silicon

*Aluminium* (Figures A4.35 and A4.36): Aluminium concentration is strongly controlled by pH and is generally very low under neutral conditions. The greatest Al concentrations in Lawlers groundwaters are observed in the Gt. Eastern/Caroline area, possibly due to the granitic rocks in this area, and at Four Corners, particularly in the centre of the mineralized area (Figure A4.36). This is consistent with data from Granny Smith (Gray, 1993a) and elsewhere (Gray, unpublished data) that suggest that groundwaters contacting shear structures or mineralized rocks have anomalously high Al concentrations (when pH effects are taken into account). This enrichment may be due to Al release from feldspars or other minerals by transient acid conditions produced during sulphide oxidation.

*Gallium* (Figures A4.37 and A4.38): Gallium has a similar ionic radius to Al ( $\text{Ga}^{3+}$  - 0.62 Å,  $\text{Al}^{3+}$  - 0.51 Å) and therefore is almost always found substituted in Al minerals (Goldschmidt, 1954). The Ga groundwater distribution closely matches that of Al (Figures A4.35 and A4.36); the correlation between enhanced Ga and mineralization at Four Corners is even more evident than for Al. In addition, Ga



shows a significant groundwater enhancement at Hidden Secret. Gallium differs from Al in that it can occur in sulphide minerals, hence the additional Ga enrichment at Hidden Secret may reflect the preferential dissolution of sulphides, relative to Al-bearing minerals, as appears to be the case at other sites (Gray, 1993a).

*Silicon* (Figures A4.39 and A4.40): The dissolved Si distribution at Lawlers is highly variable, possibly reflecting the large number of possible Si sources (e.g., feldspars, chlorites) and sinks (e.g., kaolinite, amorphous silica, quartz). The lower Si concentration in the southern part of Four Corners may reflect a different groundwater system (also see Sections 5.2 and 5.3).

## 5.5 First row transition metals

*Scandium* (Figures A4.41 and A4.42): Scandium is often linked with Y and REE, though by virtue of its smaller ionic radii (0.75 Å, compared with 0.86 - 1.05 Å for Y and REE), it is commonly associated with Fe<sup>3+</sup> or Al minerals and has a distinct geochemistry from REE (Fronzel, 1978). Dissolved Sc appears anomalous at Genesis, Hidden Secret and for the Gt. Eastern/Caroline groundwaters closest to the Au deposits, suggesting value for this element in exploration (also see Gibling, 1990, page 88; Gray, 1993b). However, there is no correlation between dissolved Sc and mineralization at Four Corners.

*Vanadium* (Figures A4.43 and A4.44): Limited data suggests highly variable V distribution.

*Chromium* (Figures A4.45 and A4.46): Chromium concentration at Lawlers is primarily related to lithology, with greatest concentrations at Fairyland and Turret, which are in ultramafic rocks. Similarly, the high Cr concentration in the southern part of Four Corners is probably due to the proximity of ultramafic rocks.

*Manganese and iron* (Figures A4.47 - A4.50): Manganese and Fe concentrations are greatest at Hidden Secret and in the centre of the mineralized zone at Four Corners.

*Cobalt* (Figures A4.51 and A4.52): As discussed previously (Section 3.6), Co concentration is strongly correlated with dissolved Au and there are higher Co concentrations at Hidden Secret and close to mineralization at Gt. Eastern/Caroline. As with Mn and Fe (see above), Co concentration at Four Corners is greatest at the centre of the mineralized area.

*Nickel, copper and zinc* (Figures A4.53 - A4.58): Groundwaters at Hidden Secret are enriched in Ni and, possibly, Cu and Zn. At Four Corners, the highest concentration of these elements (as with Mn, Fe and Co) is in the centre of the mineralized area. In addition, the groundwaters closest to the Au deposits in the Gt. Eastern/Caroline area have high Cu and Zn concentrations.

The correlation of most of the first row transition elements with the Au distribution may reflect the occurrence of Fe, Ni, Cu and Zn in sulphide minerals, and Co and Mn in carbonates, which then may be released during weathering (Section 4.1).

## 5.6 Yttrium and the rare earth elements

*Yttrium and Rare earth elements* (Figures A4.59 - A4.63): Concentrations of these elements are low, and only Y and the light REE gave results above detection. Hidden Secret was anomalous for the REE, while the granitic rocks in the Gt. Eastern/Caroline area showed higher than background Nd and Sm concentration. The ionic radii of Y (0.90 Å) closely matches those of the REE (0.86 - 1.05 Å), and Y has a similar behaviour to REE.

## 5.7 Second and third row transition elements, metalloids and uranium

*Molybdenum and tungsten* (Figures A4.64 - A4.66): These elements have similar co-ordination chemistry, but differ in that Mo mostly occurs as a sulphide (e.g.,  $\text{MoS}_2$ ), whereas W is usually found as oxygen compounds (e.g.,  $\text{FeWO}_4$ ; Goldschmidt, 1954; Evans *et al.*, 1978; Evans and Krauskopf, 1978). These differences may relate to the different groundwater distributions of these elements at Lawlers. Dissolved Mo is greatest in the Gt. Eastern/Caroline area, possibly related to the granitic rocks, with an enrichment in the mineralized area at Four Corners. Tungsten is strongly enriched at Hidden Secret, with no enrichment at Four Corners.

*Mercury* (Figure A4.67): No understandable patterns are observed for Hg.

*Thallium* (Figure A4.68): Thallium concentrations were low, with a possible enrichment at Hidden Secret.

*Germanium, tin and lead* (Figures A4.69 - A4.71): All these elements are present in groundwater at low concentrations. Germanium showed a weak anomaly at Hidden Secret, whereas no clear distribution patterns were observed for Sn and Pb.

*Arsenic and antimony* (Figures A4.72 and A4.73): Both elements are commonly associated with Au mineralization. Arsenic is strongly enriched at Hidden Secret and Genesis, with possible weaker anomalies close to mineralization at Gt. Eastern/Caroline and Turret. There are no data for Four Corners or Waroonga. Antimony also is anomalous at Hidden Secret, with possible weak anomalies at Genesis and Turret. Groundwaters at Gt. Eastern/Caroline and Four Corners have low Sb concentrations.

*Iodine* (Figures A4.74 and A4.75): High I concentrations are observed for groundwaters at Hidden Secret. Additionally the southern part of Four Corners has higher I concentrations than in the north.

*Uranium* (Figures A4.76 and A4.77): The highest U concentration is observed at Hidden Secret, with moderate concentrations also observed in those groundwaters at Gt. Eastern/Caroline within granitic lithologies. At Four Corners, the greatest U concentrations are observed in the south, consistent with results for other elements indicating significant groundwater differences between the south and north parts of the Four Corners area.

## 5.8 Gold

As discussed previously (Sections 3.6 and 4.3), dissolved Au concentrations (Figures A4.78 and A4.79) are greatest at Hidden Secret, Genesis and close to the Gt. Eastern/Caroline deposits. At Four Corners, there is a very poor correlation between dissolved Au and mineralization, and other elements ( $\text{SO}_4$ , Al, Ga, Fe, Co, Ni and Mo; see above and Section 5.9) give much better indications of the position of mineralization. Poor exploration responses for dissolved Au in areas of transported overburden have also been observed at Mulgarrie and at Granny Smith (Gray, 1992b, 1993a).

## 5.9 General distribution patterns

Several element associations can be related to differences in style of mineralization, lithology and hydrology:

- (i) Hidden Secret - Au, TDS,  $\text{SO}_4$ , P, Mn, Fe, Co, Ni, Y, REE, W, As, Sb, I, U, and possibly Ba, Ga, Sc, Ge;
- (ii) Genesis - Au, Sc, As and, possibly, Ni, Sb;
- (iii) mineralization at Gt. Eastern/Caroline - Au, Co and, possibly,  $\text{SO}_4$ , Sc As;

- (iv) mineralization at Four Corners -  $\text{SO}_4$ , Al, Ga, Fe, Co, Ni, Mo (though generally based on only one sample at the centre of the mineralized area);
- (v) granitic rocks at Gt. Eastern/Caroline - Al, Ga, Ba, Mn, Mo, U;
- (vi) ultramafic rocks - Cr, Cs, Sr;
- (vii) southern part of Four Corners - TDS, B, Sr,  $\text{HCO}_3$ , I, U, possibly indicating a different groundwater system in this area.

These associations are similar to those at other sites in the Yilgarn, with the principal difference being the high concentration of dissolved Au ( $0.4 - 41 \mu\text{g/L}$ ), which is up to an order of magnitude greater than elsewhere, and the apparent high concentrations of Co. Differences in the chemical "signature" of the various deposits may be related to the differing styles of Au mineralization (Section 2.1.3). The multi-element signature of the concealed Four Corners deposit has possible exploration significance, but the "anomaly" is restricted to one sample in the centre of the mineralized zone and comprises dominantly lithophile elements. The Au content is low. The groundwater anomaly is thus less than 250 m in diameter, except for  $\text{SO}_4$  (Figure A4.16), which is more widely dispersed anomaly, possibly due to its high mobility.

## 6 DISCUSSION AND CONCLUSIONS

The groundwater data at Lawlers have significance, being from an area north of the Menzies line with neutral, low salinity groundwaters, in contrast with previous studies of dominantly saline groundwaters further south. The low salinities and the marked divergence from sea water ion ratios for Lawlers groundwaters (Section 3.4), suggest that major ion concentrations are strongly controlled by local lithological or hydrological factors. Elements that appear to be controlled by mineral equilibration in some or all groundwaters (Sections 3.4 and 3.5) are Ba (barite equilibration), Ca, Mg and  $\text{HCO}_3$  (carbonate equilibration), Mn (rhodochrosite), Sb [ $\text{Sb}(\text{OH})_3$ ], Pb and V ( $\text{Pb}_2\text{V}_2\text{O}_7$ ). Major and minor element data (Section 5) suggests a significant difference between groundwaters in the south and north parts of Four Corners. The various groundwater element association with differences in style of mineralization, lithology and hydrology are summarized in Section 5.9.

The most marked feature of the Lawlers groundwaters are the extremely high Au concentrations (Section 3.6), with the highest observed concentration of  $40 \mu\text{g/L}$  being about ten times greater than previously reported values. These high concentrations are correlated with highly anomalous Co concentrations at Hidden Secret and in the Gt. Eastern/Caroline pits area but not at Genesis. Under the groundwater conditions observed at this site, the most likely mechanism for dissolution is expected to be as the thiosulphate complex  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  (Eqn. 2), with the thiosulphate being generated during neutral sulphide oxidation (Eqn. 1). This requires the presence of minerals such as primary carbonates which can neutralize protons generated by the oxidation of the sulphide group (Eqns. 3 and 4). At Hidden Secret, limited data suggests that higher Au concentrations are correlated with increased Mg, Ca,  $\text{SO}_4$  and  $\text{HCO}_3$ , consistent with enhanced Au concentrations being observed in zones of significant neutral sulphide oxidation.

Differences in the mineralization "signature" at the various sites may be related to the differing type of Au mineralization (Section 2.1.3). The Gt. Eastern/Caroline and Hidden Secret groundwaters have groundwater signatures similar to other mineralized sites elsewhere in the Yilgarn, with anomalies in a range of chalcophile and other pathfinder elements. In contrast, the Genesis groundwaters have a particularly limited (and distinctive) 'signature', being anomalous in only Au, Sc and As. This may be due to the Genesis ore deposit being hosted in quartzite, with disseminated arsenopyrite. At the Four Corners area, which is covered with extensive transported overburden, there are anomalous concentrations of varying elements (but not Au), though the anomaly is generally based on one sample

in the centre of the mineralized area, with size of the groundwater anomaly appearing to be less than 250 m diameter. The exception to this is  $\text{SO}_4$ , which has a more disperse anomaly.

There is some potential for the use of hydrogeochemistry for Au exploration in the Lawlers area. Dissolved Au concentrations are very high, relative to other sites and there appears to be an additional multi-element signature. This signature varies for the four mineralized zones (Section 5.9), possibly related to differences in the underlying mineralization (Section 2.1.3). The groundwater Au anomalies are highly localized (*i.e.*, little dispersion in the groundwater) and not observed for the areas of appreciable overburden such as Four Corners, similar to equivalent sites with neutral groundwater and transported overburden (Gray, 1992b, 1993a). This suggests that in such areas dissolved Au is not a useful exploration tool, though other elements (Mn, Co, Ni, Zn, Mo, Tl, Pb and As at Granny Smith and  $\text{SO}_4$ , Al, Ga, Mn, Fe, Co, Ni and Mo at Lawlers) have higher concentrations in mineralized areas and appear to have potential as soluble pathfinders. The major similarities between the elements enhanced with mineralization in areas of overburden at Granny Smith and Lawlers, and with mineralization in residual areas (Gray, 1990, 1991, 1992a, 1993a,b) suggests that particular elements could be used for exploration using groundwater.

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