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# **INVESTIGATION OF HYDROGEOCHEMICAL DISPERSION OF GOLD AND OTHER ELEMENTS IN THE WOLLUBAR PALAEODRAINAGE, WESTERN AUSTRALIA**

## **Volume 2 - Appendices**

*D.J. Gray*

**CRC LEME OPEN FILE REPORT 33**

September 1998

(CSIRO Division of Exploration Geoscience Report 387R, 1993.  
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.

This report (CRC LEME Open File Report 33) is a first revision of CSIRO, Division of Exploration Geoscience Restricted Report 387R, first issued in 1993, which formed part of the CSIRO/AMIRA Project P241A.

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

The Publication Officer, CRC LEME, CSIRO Exploration and Mining, PMB, Wembley, WA 6014, Australia. Information on other publications in this series may be obtained from the above or from <http://leme.anu.edu.au/>

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## PREFACE

The Wollubar palaeodrainage is an extensive Tertiary channel that crosses over significant mineralized areas, in particular the Boulder-Lefroy shear, which is the host for several Au deposits. It therefore represents a field area where the hydrogeochemical relationships between mineralized Archaean rocks and an overlying palaeochannel can be investigated. The palaeochannel waters were also acid, thereby offering a comparison with other work on the hydrogeochemistry of a neutral palaeodrainage system adjacent to mineralized rocks. The site was considered suitable for testing the potential for acid palaeochannel groundwaters as an exploration medium at this site, and to investigate present-day dispersion processes in groundwater within such a system.

Hydrogeochemistry may be of value for several reasons:

- (i) narrow geochemical anomalies may have broader groundwater signatures;
- (ii) a structure just missed by drilling may still have a hydrogeochemical signature in the sampled groundwater;
- (iii) 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;
- (iv) hydrogeochemical studies may expand information on how various materials are weathering, which may enhance understanding of saprolite geochemistries.

This report details a study on the potential for water sampling in exploration, and of hydrogeochemical processes, at the Wollubar palaeochannel. The study provides a basis for evaluating the potential of hydrogeochemical exploration in this environment.

C.R.M. Butt,  
Project Leader.  
May, 1993

## ABSTRACT

The hydrogeochemistry, and the usefulness of groundwater as an exploration medium, was investigated for a 30 km length of the Wollubar palaeodrainage, an acid groundwater system that passes over mineralized Archaean rocks. Limited sampling was also conducted at the Golden Hope pit, about 1.5 km north of the palaeodrainage.

The Golden Hope groundwaters are very similar to deep waters from other mineralized sites, having neutral pH, low to moderate Eh and anomalous concentrations of Fe,  $\text{SO}_4$  (from sulphides), Mg, Ca, Sr and  $\text{HCO}_3$  (from carbonates). These data, and speciation results indicating groundwater equilibration with calcite, dolomite and magnesite, suggest that sulphides are dissolving at the weathering front, with the resultant acidity being neutralized by carbonate dissolution. Other minerals that appear to be in equilibrium with some or all of the Golden Hope groundwaters are gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), barite ( $\text{BaSO}_4$ ), amorphous alumina  $[\text{Al}(\text{OH})_3]$  and ferrihydrite  $[\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}]$ . In addition, the groundwaters at Golden Hope are enriched in Ga, Mo, W, Ag, Hg, Tl, I,  $\text{PO}_4$  and Cs. These elements (possibly with As, which was not determined) may also have value for exploration. Most of these elements appear to be sulphide associated, so they may not be directly related to Au. However, a system for easily pinpointing sulphide enrichments may still have exploration value.

The groundwaters at Golden Hope are different from other mineralized sites in that they are not Au-rich. The reasons for this difference are not clear, because in all known respects these groundwaters should be just as effective in dissolving Au, as a thiosulphate complex, as other sites previously investigated. If dissolved Au is to be used as an exploration tool, it is critical to understand why strong groundwater enrichments are only occurring at some sites.

Total salinity, K and Br data indicate that groundwaters in the palaeochannel to the west and to the east of the main Boulder-Lefroy shear are hydrochemically distinct. This is consistent with the proposal that the two systems join near the shear and then flow south into Lake Lefroy. The palaeodrainage system is acid, with pH varying from near 6 at the northern part of the study area down to 3 in the western arm. In general, results for Wollubar closely matched observations at other sites with acid groundwaters, with the major difference that the Wollubar groundwaters were Fe-rich, and therefore tended to have lower Eh values. The mineral phases that appear to be equilibrating with some or all of the groundwaters, and the elements being controlled are:

- (i) fluorite (F);
- (ii) gypsum (Ca);
- (iii) barite (Ba);
- (iv) amorphous silica, for  $\text{pH} < 4$  (Si);
- (v) jurbanite, for  $\text{pH} < 5$  (Al);
- (vi) amorphous alumina, for  $\text{pH} > 5$  (Al);
- (vii) ferrihydrite, for  $\text{pH} > 4.5$  (Fe);

With the exception of Au, for which speciation analysis works poorly, the minor elements were undersaturated with respect to their least soluble mineral phase, indicating that dissolution has occurred slowly and/or that concentration is being limited by other mechanisms such as sorption on, or co-precipitation with, iron oxides. Most metals, and particularly the base metals (other than the higher charge ions Al, Sc, Cr and U), showed no clear relationship with pH, possibly because their abundance was also affected by other hydrogeochemical or lithological factors. The concentration of REE is very high at Wollubar, both in the palaeodrainage and where acid waters are directly contacting Archaean rocks, being at least 5 times greater than for any other known surface water or groundwater in the world.

The palaeodrainage samples adjacent to the main Boulder-Lefroy shear showed particularly anomalous characteristics, being enriched in a similar "sulphide suite" as for the Golden Hope samples (Ga, Fe, Mo, W, Ag, Hg and Tl), in acid soluble elements (Sc, Y, REE and, relative to the observed pH, Al, Si and U) and also Au and Pb. This may represent acid weathering of a similar mineralized material to that at Golden Hope, and indicates that even high flow palaeochannel groundwaters can have solution characteristics relating to underlying mineralization.

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## 1 INTRODUCTION

This report describes an extensive investigation of the hydrogeochemistry of a 30 km length of the Wollubar palaeodrainage system, with additional, limited, sampling at Golden Hope pit about 1.5 km north of the palaeodrainage. The objectives of the investigation were:

- (i) to provide information on whether groundwater can successfully transport Au and other elements in an acid palaeodrainage environment;
- (ii) to investigate the hydrogeochemical relationships between mineralized Archaean rocks and an overlying palaeochannel;
- (iii) to yield data on geochemical dispersion processes in the area;
- (iv) to contribute to a groundwater database on characteristics of Yilgarn groundwaters, and to enhance our understanding of groundwater processes in mineralized zones.

The Wollubar system was selected for a number of reasons:

- (i) it lies in the Kalgoorlie district and therefore expands the database on this area;
- (ii) there are major increases in groundwater salinity along the flow path, enabling study of the effect of salinity changes on the chemistry of Au and other elements;
- (iii) the palaeodrainage system flows across several different lithological units, with possible changes in the groundwater composition;
- (iv) the system passes directly over the Boulder-Lefroy shear, host to a series of semi-continuous Au deposits, and other Au-rich areas, which may result in the release and transport of Au in the groundwater.

The scope of the proposed study included the effect of salinity and/or pH changes on the chemistry of Au and other trace elements, effect of underlying lithology on the observed water chemistry, thermodynamic modelling, mapping of the data, and comparison with results from other Yilgarn waters.

## 2 STUDY SITE AND METHODS

### 2.1 Site characteristics

#### 2.1.1 *Geology and mineralization*

The investigation area is located 40 km southeast of Kalgoorlie at latitude 31°S, longitude 121°30'E (Figure 1). The geology of the New Celebration Au deposits, which lie in the north and centre of the study area, is described in detail in Norris (1990), with the Mount Martin Au deposit, which lies in the northwest part of the study area, being briefly discussed in Washausen (1990). A summary is given below.

The New Celebration line is a series of semi-continuous deposits hosted by the Boulder-Lefroy shear. These include the Celebration, Mutooroo, Villers Bretonneux and Hampton Boulder deposits to the north, and the Jubilee and Golden Hope deposits further south. The area is underlain by a suite of Archaean greenstone similar to the Kalgoorlie sequence, with all units in the sequence having mineral assemblages suggesting upper greenschist metamorphism. Stratigraphic units have been folded to form a tight, steeply north plunging anticline. This fold is truncated along the axial plane by the Boulder-Lefroy shear zone (Figure 1), which extends from north of Kalgoorlie to south of Kambalda and is considered to be a deep seated structure which has been active over a long period of geological evolution. Differential movement between stratigraphic units has resulted in strong shearing of most contacts.



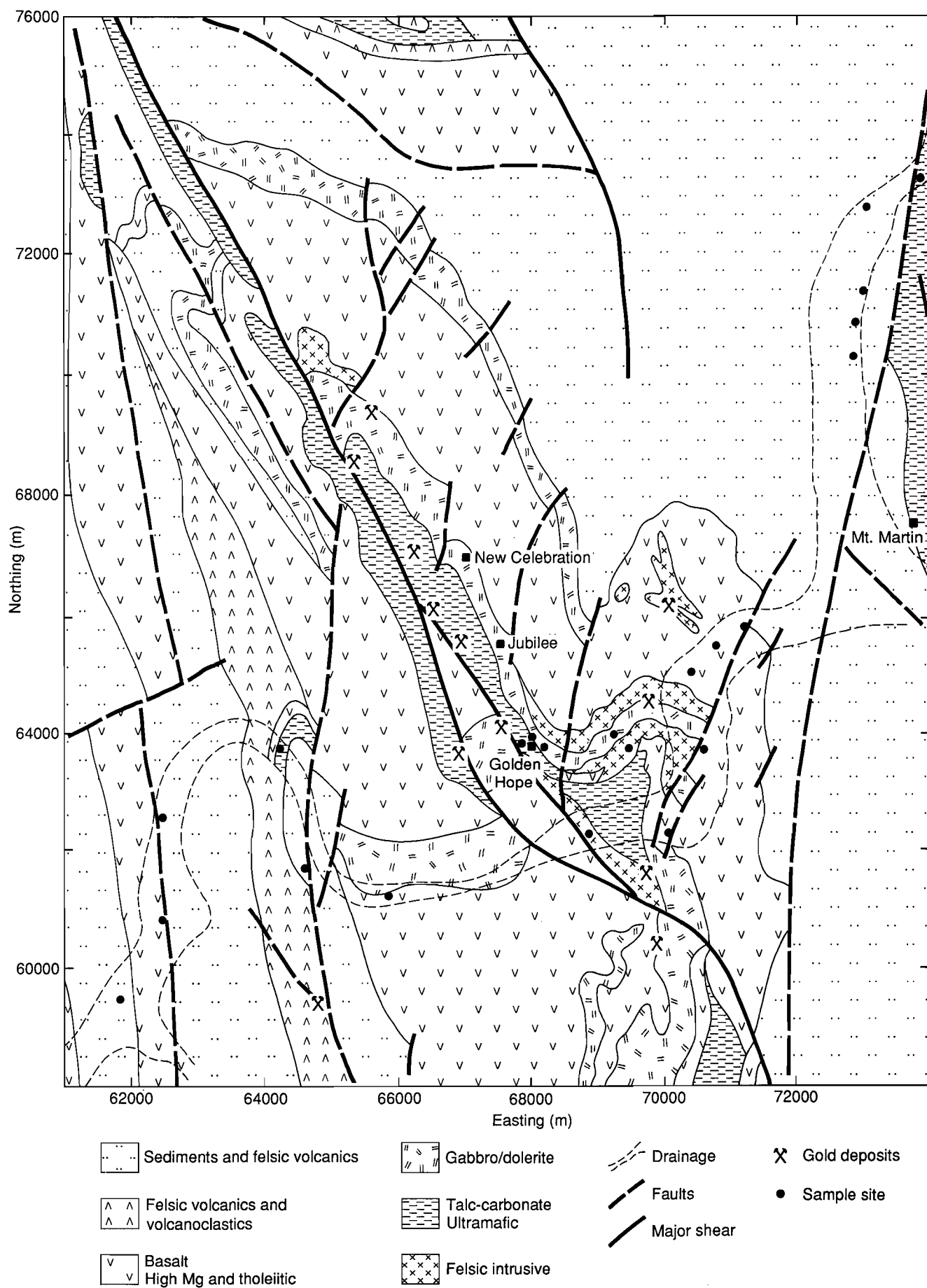


Figure 1: Geology of the Wollubar study area (courtesy, Newcrest Mining Ltd.).

Within the study area, Au mineralization is observed in most stratigraphic units. Structure exerts an overriding control on mineralization, with the properties of some lithologies providing more favourable hosts. Properties of particular importance include brittleness, permitting development of permeable fractures and thereby allowing access for hydrothermal solutions, and the availability of Fe to assist in the formation of sulphide minerals and precipitation of Au from solution. Of the mineral resources defined to date, most fall into three categories:

- (i) porphyry-related mineralization;
- (ii) shear-controlled mineralization within basic volcanics and intrusives;
- (iii) quartz vein-related mineralization within basic volcanics and intrusives.

### 2.1.2 Geomorphology

Recent studies on the geomorphology and groundwater characteristics have been conducted by the Geological Survey of Western Australia (GSWA; Commander *et al.*, 1992). The area now has a low relief, but in the early Tertiary was incised by an drainage system (the Roe Palaeodrainage) that drained eastwards into the Eucla Basin (Figure 2). The early Tertiary sediments generally consist of a basal fluvial sand overlain by lacustrine clay and concealed by Quaternary sediments. These sediments have been subdivided into the Wollubar Sandstone and the Perkolilli Shale. The Wollubar Sandstone rests unconformably on Archaean rocks and is overlain conformably by the Perkolilli Shale. In the Kalgoorlie region these formations occur only in the palaeochannels and do not outcrop.

The Wollubar Sandstone consists of very coarse to fine quartz sand, with minor amounts of conglomerate, clay, silt, carbonaceous silt and lignite. Traces of ferromagnesian minerals occasionally occur as accessory minerals; pyrite occurs at the base of the sand northeast of the study area. The base of the Sandstone is frequently conglomeratic, and may contain angular quartz pebbles up to 100 mm. The formation has a maximum thickness of 38 m in the region. The Sandstone has been palynologically dated as late Middle to early Late Eocene. It correlates lithostratigraphically with the Hampton Sandstone, which occurs in the western part of the Eucla Basin (Lowry, 1970) and extends into the Lefroy Palaeodrainage (Jones, 1990).

The Perkolilli Shale consists of clay with minor beds of sandy clay. The clay is generally plastic except near the surface, where it is weathered and friable. Ferruginous pisoliths up to 5 mm in diameter are scattered through the clay. They are more common near the base of the formation and are believed to have formed *in situ*. The Perkolilli Shale rests conformably on the Wollubar Sandstone, commonly with a sharp contact indicating a rapid change of facies but, in some cases, with alternating bands of sand and clay forming a transitional contact. An early Late Eocene age is assumed. Lithologically, the Perkolilli Shale correlates with the Pallinup Siltstone of the Plantagenet Group and the lacustrine facies of the lower unnamed unit of the Eundynie Group (Griffin, 1989). The Perkolilli Shale is an age equivalent of the Princess Royal Spongolite in the Lefroy Palaeodrainage (Jones, 1990). The formation has a maximum thickness of 39 m in the Kalgoorlie area and is unconformably overlain by Quaternary deposits, with the contact generally between 4 and 6 m below the surface.

These sediments, principally the Perkolilli Shale, have been modified by *in situ* weathering, particularly the processes involving silicification, ferruginization and calcification. The lack of clastic sediments younger than the mid Miocene may indicate that the palaeodrainages had infilled and ceased flowing by that time.

Commander *et al.* (1992) suggest that major weathering postdates incision of the drainage system, with an Oligocene age for the lateritization (Bunting *et al.*, 1974; van de Graaff *et al.*, 1977). The Eocene valley-fill sediments appear to lie in the lowest parts of the drainage system. The palaeodrainage cross-sections are generally V-shaped, and subsequent lateral erosion of the valley sides above the preserved Tertiary sediments has occurred. Modification of the Tertiary drainage pattern has taken place at

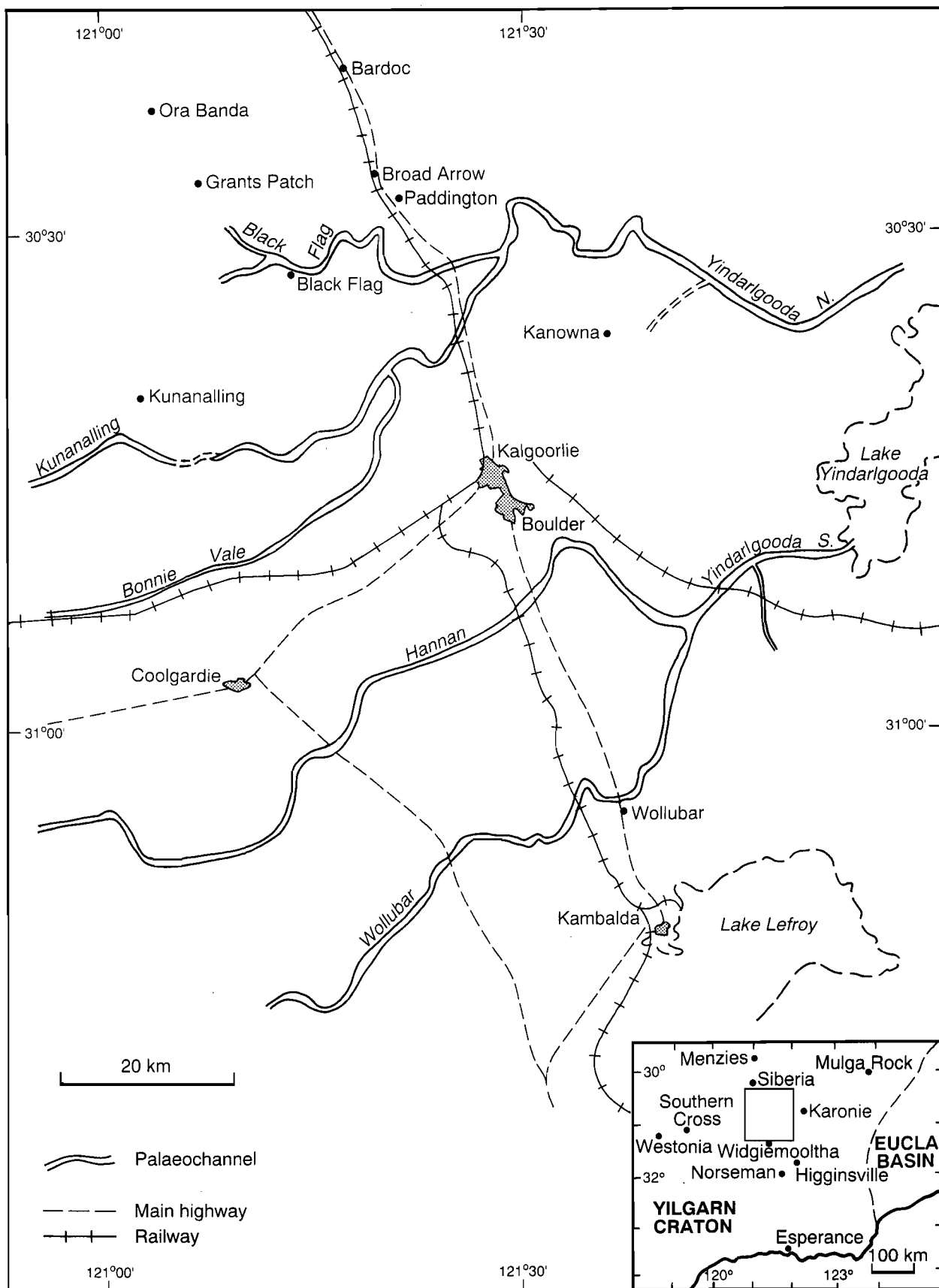


Figure 2: Major palaeochannels in the Kalgoorlie region (modified from Commander *et al.*, 1992, courtesy GSWA).

Wollubar by erosion of the catchment divide and diversion of runoff into Lake Lefroy (Section 2.1.3), which lies approximately 20 km south of the study area.

### 2.1.3 General groundwater characteristics

The region has a semi-arid climate with a large temperature range, and an average annual rainfall of about 250 mm. Rainfall is highest in the winter, but intense rainfall can occur sporadically in summer as a result of tropical cyclones. Potential evaporation totals 2400 mm/year and greatly exceeds rainfall for most of the year.

Groundwater recharge in the study area is low due to the low rainfall, high evaporation, heavy soils and well developed vegetation cover, and internal drainage. Most groundwater is saline or hypersaline; brackish groundwater occurs only in small elevated areas where recharge conditions are favourable. The principal aquifer in the region is the Wollubar Sandstone, in the palaeodrainages. The Sandstone is in the topographically lowest position and contains only saline and hypersaline groundwater. The Wollubar Sandstone aquifer is unconfined only in the upper reaches of the palaeodrainage, and confined in the study area by the relatively impermeable Perkolilli Shale.

A conceptual model of the hydrogeology of the region is discussed in Commander *et al.* (1992) and illustrated diagrammatically in Figure 3. The essentials of this interpretation are that: the recharge from rainfall and local runoff is extremely small; cyclic salts from rainfall are concentrated and, when recharge occurs, give rise to mainly saline recharge into the Archaean bedrock and upstream parts of the palaeochannels. The palaeochannels are regional sumps receiving groundwater from the Archaean bedrock. They discharge from the region principally by evaporation from the salt lakes. Groundwater outflow from the region represents a very small proportion of the components of the water balance.

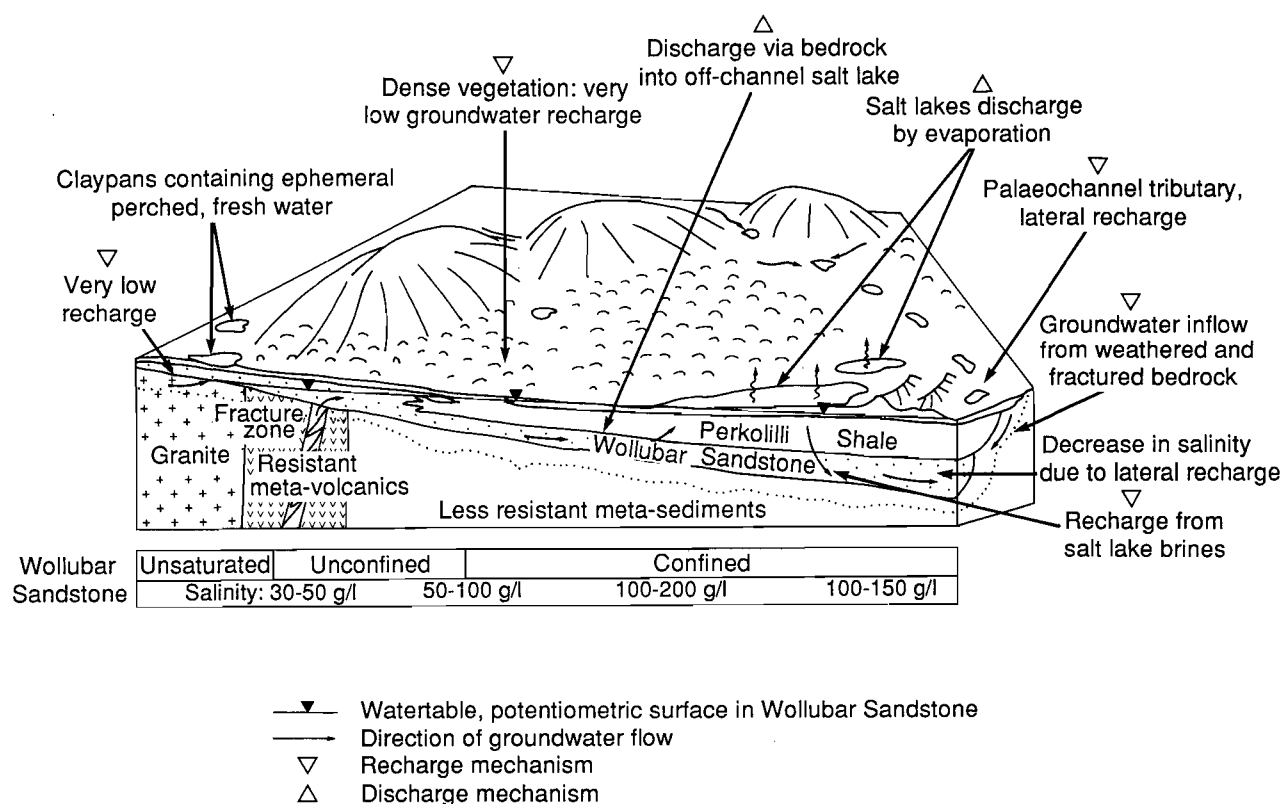


Figure 3: Conceptual model of the hydrogeology of the Kalgoorlie region (from Commander *et al.*, 1992, courtesy GSWA)

The playas (e.g., Lake Lefroy to the south, and Lake Yindarlgooda to the east, of the study area; Figure 2) are important for the removal of water by evaporation and the concentrating of salts, thereby increasing the groundwater salinity. The salty groundwater does not appear to be connate, but saline water that has accumulated over at least a few hundred thousand years. It is not certain whether salt is being accumulated or discharged under the present hydrological regime.

Reversal of the groundwater flow has occurred in the lower part of the Wollubar palaeochannel, near the intersection of the palaeodrainage with the Boulder-Lefroy shear (Figure 4). In this area, the confining bed and the upper part of the Wollubar Sandstone have been removed by erosion, the water-table is close to the surface, and the potentiometric heads indicate groundwater discharge. Groundwater derived from Lake Yindarlgooda (Figure 2) is flowing "upstream" in the palaeochannel to discharge to the surface at Wollubar, and ultimately into Lake Lefroy. This is discussed further in Section 3.3.

The palaeochannel, and others within the Kalgoorlie area, is a major source of water for mining operations, with 4000 million litres expected to be abstracted per year from this area for the next 10 years (Commander *et al.*, 1992). Further research on the groundwater resource at this and other areas near Kalgoorlie has been conducted within CSIRO (Groundwater Recharge in the Kalgoorlie Region: AMIRA Project P321 / MERIWA M146).

## 2.2 Sample collection and analysis

Groundwaters were sampled at various times in 1991 and 1992, along about 30 km of the Wollubar palaeodrainage system (Figure 5). Three samples from the Golden Hope mine and two samples between Golden Hope and the palaeodrainage were bailed from bore holes using a pump-sampler; the other 17 samples were from supply bores and obtained by pumping (Table 1).

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 0.45  $\mu\text{m}$  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 Na, Mg, Ca, K,  $\text{SO}_4$ , Sr, Ba, Al, Si, P, Ti, Cr, Mn, Fe, Co, Ni, Cu and Zn by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) 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.

In addition, about 50 mL of the filtered water was collected separately, and analysed by Ion Chromatography, for Cl, Br and  $\text{SO}_4$ , using a DIONEX AS4A column under standard eluent conditions (Dionex, 1985) with a conductivity detector, and for I using a DIONEX AS5 column under standard eluent conditions with an electrochemical detector.

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 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 using this pre-concentration system permits successful analyses of waters for these elements at low concentrations and high salinities. Calibration of the method was obtained by shaking Au standards of varying concentrations, and in varying salinities, with activated carbon (Gray, unpublished data).



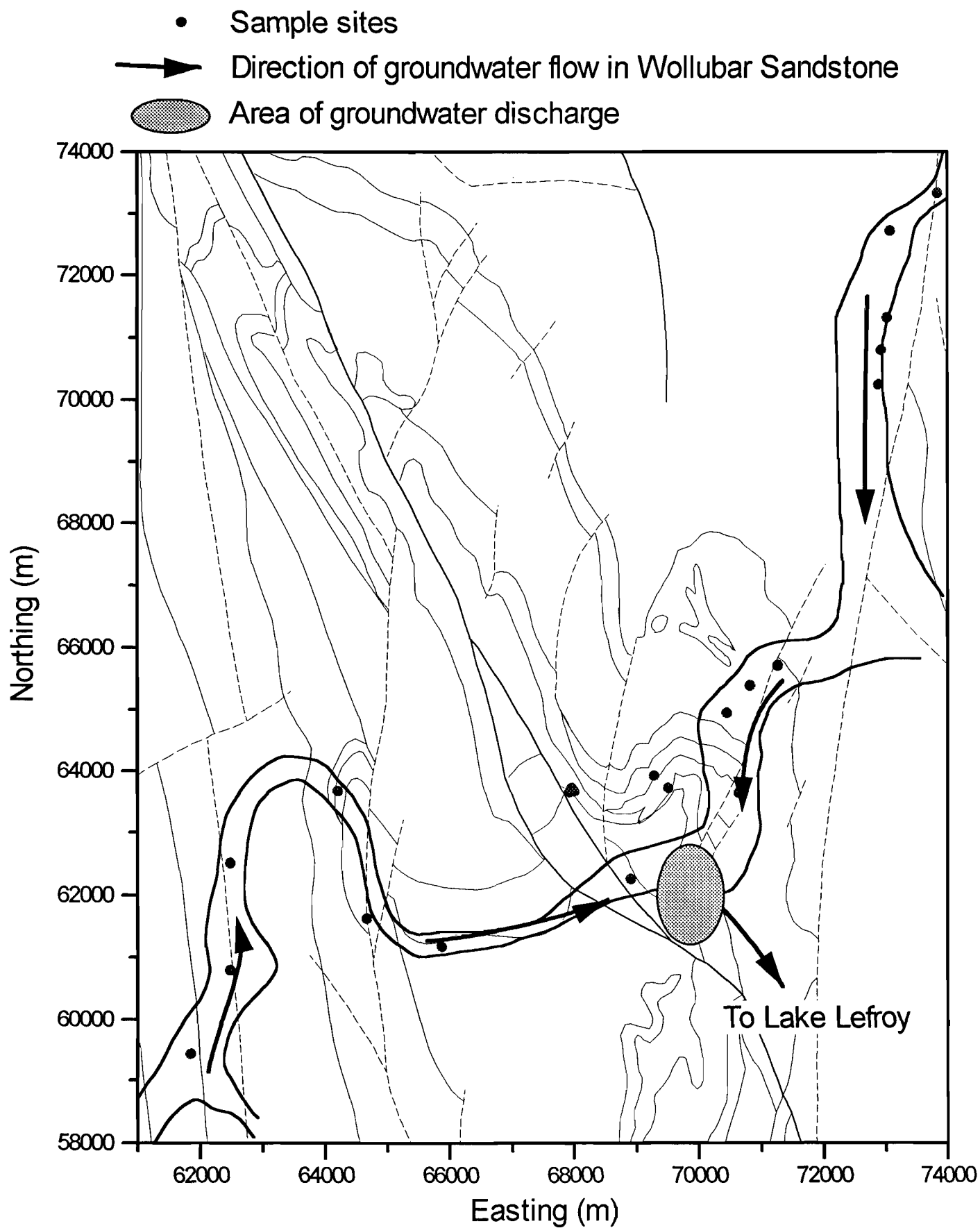


Figure 4: Schematic diagram of water flow in Wollubar palaeodrainage.

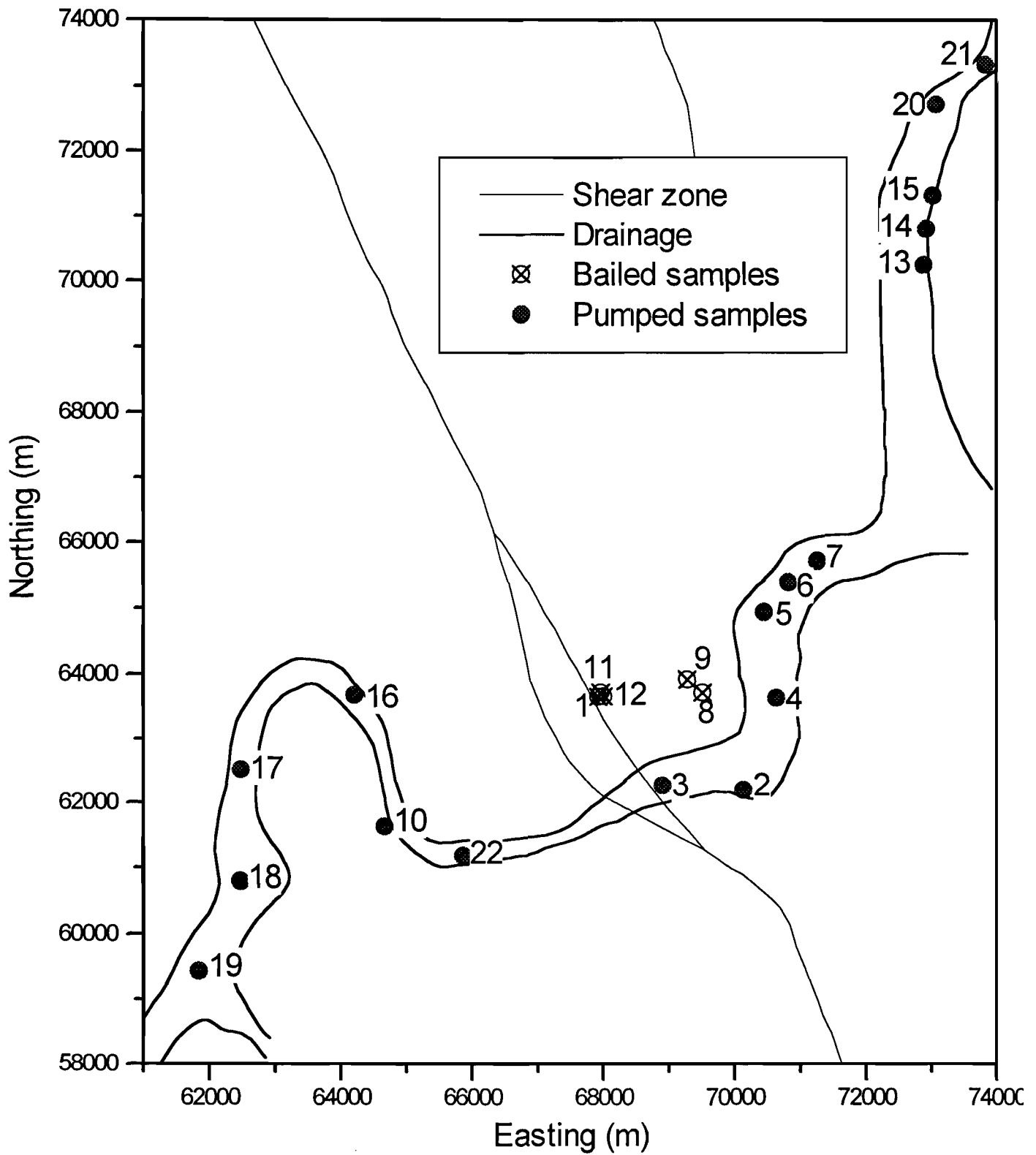


Figure 5: Sample locations at Wollubar.

Table 1: Sample details for Wollubar water samples.

Sample No.	Hole Name	Easting (m)	Northing (m)	Sampling Method	Water Table (m)	Sampling Depth (m)
Woll1	Chlorite Schist-Golden Hope	67920	63652	Bailed	34	44
Woll2	HW64	70123	62194	Pumped	nd	nd
Woll3	HW51	68894	62261	Pumped	nd	nd
Woll4	HW1	70625	63631	Pumped	nd	nd
Woll5	HW4	70443	64947	Pumped	nd	nd
Woll6	HW7	70816	65396	Pumped	nd	nd
Woll7	HW6	71255	65712	Pumped	nd	nd
Woll8	Poly 1	69506	63718	Bailed	nd	nd
Woll9	Uncased 1	69279	63921	Bailed	5.5	8
Woll10	JP1	64666	61626	Pumped	nd	nd
Woll11	Shear Zone - Golden Hope	67955	63717	Bailed	39.5	49.5
Woll12	Ultramafic - Golden Hope	68000	63662	Bailed	40	42
Woll13	NB-1	72879	70244	Pumped	nd	nd
Woll14	NB-2	72914	70800	Pumped	nd	nd
Woll15	NB-3	73012	71314	Pumped	nd	nd
Woll16	JP-5	64200	63677	Pumped	nd	nd
Woll17	JP-2	62477	62512	Pumped	nd	nd
Woll18	JP-4	62472	60792	Pumped	nd	nd
Woll19	JP-3	61846	59436	Pumped	nd	nd
Woll20	NB-4	73061	72727	Pumped	nd	nd
Woll21	NB-5	73830	73335	Pumped	nd	nd
Woll22	Bore Pump A	65868	61177	Pumped	nd	nd

nd not determined

The accuracy's of the total analyses were confirmed by measuring the cation/anion balance (*i.e.*, total cationic charge less total anionic charge, all divided by total charge). The balances were all better than 4%, and in most cases better than 2%, indicating good analytical accuracy for the major elements.

### 2.3 Speciation analysis

Speciation analysis involves inputting of solution data into a computer program that calculates particular solution parameters. This is commonly done using the program PHREEQE (Parkhurst *et al.*, 1980), which is described in detail in Gray (1990) and Gray (1991). Because of the high salinity of some of the Wollubar samples, ion pairing effects become important and programs using the specific ion interaction model known as the Pitzer equations need to be used. The program used was PHRQPITZ (courtesy United States Geological Survey) which gives complete data for Na, K, Mg, Ca, Cl, HCO<sub>3</sub> and SO<sub>4</sub>, and partial corrections for Sr, Ba, Fe and Mn. A sample output from PHREEQE is given in Appendix 3.

These programs are used to calculate the solubility indexes (SI) for a number of mineral phases for each water sample. If the SI for a mineral equals zero (empirically from -0.5 to 0.5 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 environmental effects. Thus, for example, 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

Analytical results are compiled in Appendix 1, and are discussed in detail below. The total dissolved solids (TDS), a measure of groundwater salinity, were calculated from the major element contents. In the following sections the samples from the Golden Hope pit (Woll1, Woll11 and Woll12), are treated separately from the other samples, which are designated as from the Wollubar palaeochannel.

#### 3.1 Comparison with results from other Yilgarn waters

Averaged elemental data for the Wollubar and Golden Hope groundwater samples are given in Tables 2 and 3. Also listed are data for sea water (taken from Weast *et al.*, 1984) and the averaged data for five other sites previously investigated:

- (i) Mulgarrie (samples Mul2 - Mul7), a neutral palaeodrainage system crossing mineralized rocks about 40 km north of Kalgoorlie (south Yilgarn; Gray, 1992b);
- (ii) Yalanbee, a non-mineralized area which lies some 50 km east of the western edge of the Yilgarn Block;
- (iii) Boags, a gold deposit at Bottle Creek, located 210 km north north-west of Kalgoorlie (central Yilgarn; Gray, 1992a);
- (iv) Mount Gibson, a gold deposit about 100 km north-east of Dalwallinu (central-west Yilgarn; Gray, 1991);
- (v) Panglo, a gold deposit some 30 km north of Kalgoorlie (south Yilgarn; Gray, 1990).

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 Wollubar, Golden Hope and other sites are plotted *versus* TDS or *versus* pH in Appendix 2, Figures A2.1 - A2.50. 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. Where the sea water line is not visible, 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.

Specific results will be discussed in the following sections.

Table 2: Averaged major element compositions of Wollubar and Golden Hope groundwaters, with mean results from other sites given for comparison.

	Wollubar (19) #		Golden Hope (3)		Mulgarrie	Yalanbee	Boags	Mount	Panglo	Sea
	Mean	Sd Dv@	Mean	Sd Dv	(6)	(3)	(2)	Gibson (50)	(50)	water
pH	4.5	0.9	6.35	0.13	6.8	4.7	6.6	6.5	4.9	nd
Eh (mV)	380	110	200	50	180	300	160	310	490	nd
Na *	0.31	0.01	0.27	0.01	0.29	0.28	0.25	0.32	0.32	0.31
Mg *	0.040	0.002	0.062	0.005	0.052	0.057	0.052	0.033	0.032	0.04
Ca *	0.006	0.002	0.013	0.010	0.012	0.02	0.032	0.009	0.008	0.012
K *	0.0032	0.0027	0.0057	0.0023	0.0041	0.003	0.0092	0.0112	0.0008	0.0112
Cl *	0.56	0.01	0.52	0.01	0.54	0.6	0.47	0.53	0.59	0.56
SO <sub>4</sub> *	0.073	0.013	0.126	0.012	0.103	0.045	0.172	0.075	0.053	0.065
Br *	0.0012	0.0007	0.0019	0.0002	0.0016	0.0016	0.0024	0.0017	0.0005	0.0019
HCO <sub>3</sub>	20	30	690	230	398	nd	620	260	50	142
TDS	73000	25000	45000	5000	41800	8100	21000	24000	84000	34000

# Numbers in brackets denote the number of samples taken at each site.

@ Standard Deviation.

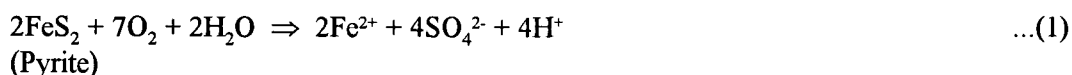
\* For the elements Na, Mg, Ca, K, Cl, SO<sub>4</sub> and Br, the ratio of the element concentration to TDS is used rather than the concentration. (See Section 3.3 for details.)  
Other concentrations in mg/L (ppm).

nd not determined

### 3.2 Acidity and oxidation potential

An Eh-pH plot of waters from Wollubar, Golden Hope and other sites is shown in Figure 6. The samples from Golden Hope are near neutrality, with a low Eh, which is similar to other deep mine waters, specifically Boags (Gray, 1992a) and some of the Mt. Gibson samples (Gray, 1991). The Wollubar groundwaters range from near neutrality (pH 6) to very acid (pH 3), which is similar to the pH range for shallow waters obtained from Panglo (Gray, 1990), although the Wollubar samples have generally lower Eh than Panglo (Figure 6). This is presumably related to the higher Fe concentrations in the Wollubar groundwaters (Figure 7), because Fe is generally present in solution as the reduced Fe<sup>2+</sup> form, which will maintain low Eh conditions.

The dissolved Fe may be derived from the first stage of the oxidation of pyrite and other sulphide minerals:



Where sulphides oxidize under neutral conditions, significant concentrations of the intermediate sulphur compounds thiosulphate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) and sulphite (SO<sub>3</sub><sup>2-</sup>) are commonly produced (Granger and Warren, 1969; Goldhaber, 1983; Webster, 1984):



Such conditions match the Golden Hope groundwaters and, to a lesser degree, some of the least acid Wollubar samples. This is of potential importance for the groundwater mobility of Au, as discussed in Section 3.5. For the other samples, the high acidity will destabilize any thiosulphate present.



Table 3: Averaged minor element compositions of Wollubar and Golden Hope groundwaters, with mean results from other sites given for comparison.

	Wollubar (19) #		Golden Hope (3)		Mulgarrie	Yalanbee	Boags	Mt. Gibson	Panglo	Sea
	Mean	Sd Dev@	Mean	Sd Dev	(6)	(3)	(2)	(50)	(50)	water
F	2.7	2.2	0.28	0.04	nd	nd	nd	nd	nd	1.3
Al	23	28	0.04	0.04	0.04	1.2	<0.01	0.3	8	0.01
Si	15	15	8	4	12	28	7	30	8	3
PO <sub>4</sub>	0.02	0.02	0.16	0.16	nd	nd	nd	nd	nd	0.21
Sc	0.001	0.001	<0.001	-	nd	nd	nd	nd	nd	nd
Ti	<0.002	-	nd	nd	nd	nd	nd	nd	nd	0.001
Cr	0.012	0.015	0.002	0.002	0.032	0.003	0.002	0.004	0.04	0.00005
Mn	3.4	2.4	0.32	0.28	4	1.2	0.035	1	3	0.002
Fe	3	3	3	5	0.04	0.7	0.07	3	0.5	0.01
Co	0.20	0.08	0.00	0.01	0.06	0.012	<0.01	0.01	0.19	0.0003
Ni	0.44	0.16	0.03	0.02	0.14	0.01	<0.01	0.01	0.26	0.005
Cu	0.06	0.06	0.04	0.03	0.021	nd	0.007	0.01	0.08	0.003
Zn	0.11	0.06	0.04	0.03	0.033	nd	0.015	0.06	0.3	0.01
Ga	0.03	0.03	0.01	0.00	nd	nd	nd	nd	nd	0.00003
As	<0.02	-	<0.02	-	<0.02	nd	0.11	nd	nd	0.003
Sr	6.2	2.5	6.7	2.9	8.4	1.6	5.9	2.4	7	8
Y	0.39	0.17	0.00	0.00	nd	nd	nd	nd	nd	0.0003
Mo	0.01	0.00	0.02	0.01	nd	nd	nd	nd	nd	0.01
Ag	<0.01	-	<0.01	-	nd	nd	nd	nd	nd	0.0003
Cd	0.003	0.003	0.002	0.001	0.002	nd	0.009	0.004	<0.005	0.0001
Sn	0.006	0.013	0.003	0.001	nd	nd	nd	nd	nd	0.003
Sb	nd	nd	nd	nd	<0.001	nd	0.17	nd	nd	0.0003
I	0.29	0.10	2.8	1.3	0.5	0.05	2.1	0.5	0.5	0.06
Cs	0.009	0.006	0.05	0.04	nd	nd	nd	nd	nd	0.0005
Ba	0.028	0.008	0.04	0.03	0.05	0.053	0.01	0.06	nd	0.03
La	0.5	0.4	0.0010	0.0005	nd	nd	nd	nd	nd	0.000004
Ce	0.7	0.7	0.0013	0.0012	nd	nd	nd	nd	nd	0.000001
Pr	0.09	0.11	0.0002	0.0002	nd	nd	nd	nd	nd	nd
Nd	0.23	0.21	0.0007	0.0003	nd	nd	nd	nd	nd	0.000002
Sm	0.04	0.03	0.0003	0.0000	nd	nd	nd	nd	nd	0.000000
Eu	0.012	0.011	0.0001	0.0000	nd	nd	nd	nd	nd	0.000000
Gd	0.040	0.025	0.0003	0.0002	nd	nd	nd	nd	nd	0.000001
Tb	0.006	0.005	<0.0001	-	nd	nd	nd	nd	nd	nd
Dy	0.027	0.018	0.0002	0.0002	nd	nd	nd	nd	nd	0.000001
Ho	0.005	0.003	<0.0001	-	nd	nd	nd	nd	nd	nd
Er	0.013	0.007	0.0002	0.0001	nd	nd	nd	nd	nd	0.000001
Tm	0.0018	0.0010	<0.0001	-	nd	nd	nd	nd	nd	nd
Yb	0.009	0.006	0.0002	0.0001	nd	nd	nd	nd	nd	0.000001
Lu	0.0015	0.0008	<0.0001	-	nd	nd	nd	nd	nd	0.000000
W	0.031	0.018	0.06	0.06	nd	nd	nd	nd	nd	0.0001
Au	0.02	0.03	0.004	0.003	0.05	nd	0.5	0.13	0.3	0.01
Hg	0.0020	0.0013	0.0039	0.0012	nd	nd	nd	nd	nd	0.0003
Tl	0.0010	0.0007	0.0006	0.0009	nd	nd	nd	nd	nd	<0.00001
Pb	0.12	0.17	0.03	0.03	0.007	nd	0.005	0.13	nd	0.00003
Th	0.0005	0.0005	0.0003	0.0002	nd	nd	nd	nd	nd	0.00005
U	0.05	0.10	0.010	0.003	nd	nd	nd	nd	nd	0.003

All concentrations in mg/L (ppm), except Au in µg/L (ppb).

# Numbers in brackets denote the number of samples taken at each site.

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

nd not determined

- not applicable

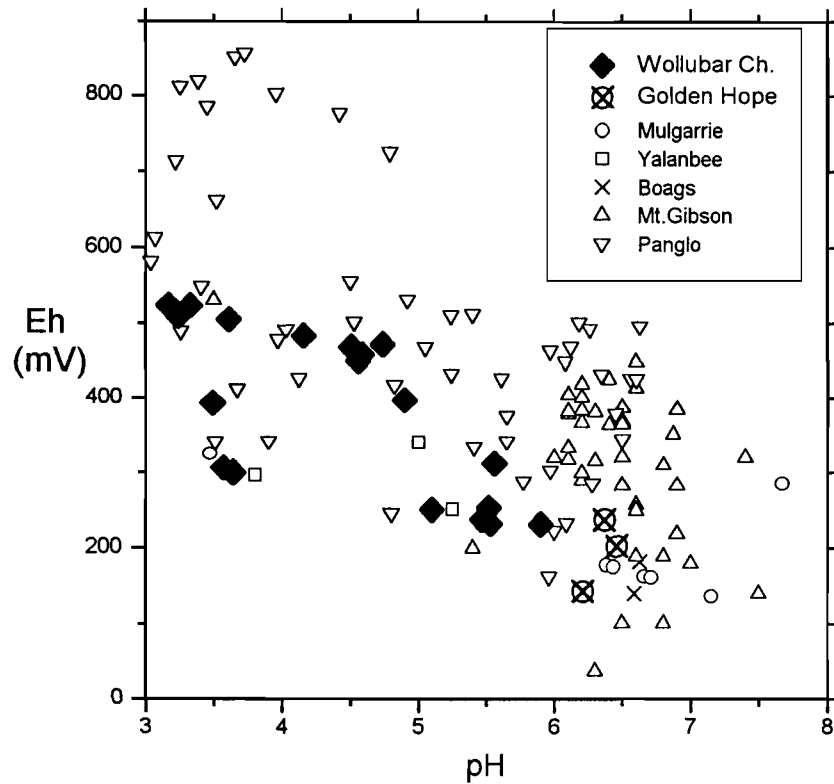


Figure 6: Eh vs. pH for groundwaters from Wollubar and other sites.

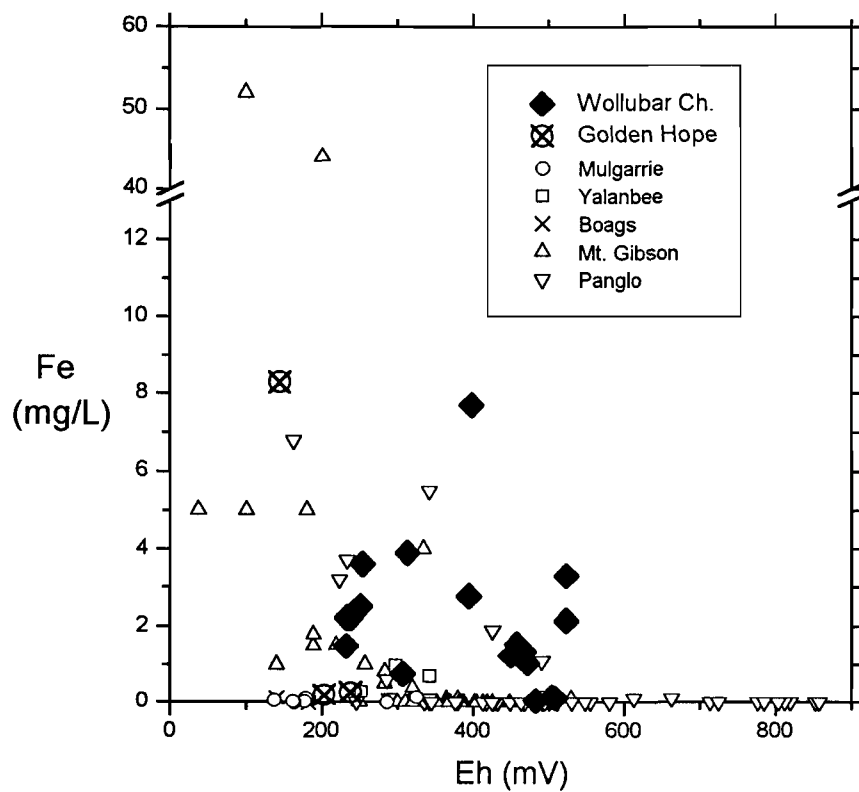


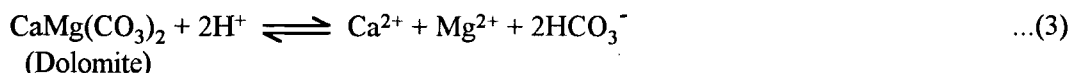
Figure 7: Dissolved Fe vs. Eh for groundwaters from Wollubar palaeochannel, Golden Hope and other sites.

### 3.3 Major ion chemistry

For the ions Na, Mg, Ca, K, Cl, SO<sub>4</sub> and Br, the ratios of the concentration divided by TDS (hereafter called the TDS ratio) are used in Table 2 rather than the concentration itself. This is because the chemistries of these ions are primarily controlled by salinization and salt precipitation effects and therefore better understood by using the TDS ratio. Additional information on the major element chemistry can be obtained by plotting the element concentration vs. TDS (Figures A2.1 - A2.8). These plots also contain the sea water value, plus the sea water line (as the dashed line) which is the relationship followed if sea water is diluted or concentrated by evaporation, with no loss or gain of elements by various solid interactions.

#### *Sodium, magnesium, calcium, chloride, sulphate and bicarbonate*

The TDS ratios of Na, Mg, Cl and SO<sub>4</sub> (though with some scatter) closely match those of sea water for the Wollubar palaeochannel samples (Figures A2.1 - A2.4), whereas waters at Golden Hope are strongly enriched in Mg, SO<sub>4</sub> and, to a lesser extent, Ca (Figure A2.7). Concentrations of HCO<sub>3</sub><sup>-</sup> are also relatively high at Golden Hope (Figure A2.9). These major element enrichments closely match results observed for deep groundwaters sampled from bore holes at Boags, which were postulated to reflect oxidation of sulphide minerals (Eqn. 1), where the acidity produced was neutralized by the dissolution of carbonate minerals such as dolomite:



leading to the observed Ca and Mg enrichment in the groundwater.

The potential for minerals precipitating or dissolving from the Wollubar and Golden Hope 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, Figures A3.1 - A3.24. 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 undersaturation and a SI greater than zero indicates the solution is over-saturated with respect to the mineral phase. Thus, the Golden Hope groundwaters appear to be saturated with respect to dolomite, magnesite and, for 1 of the 3 samples, calcite (Figures A3.5 - A3.7), consistent with the hypothesis that carbonate minerals have been dissolving.

In comparison, all of the Wollubar groundwaters are considerably undersaturated with respect to the carbonate minerals, indicating that any carbonates in the palaeochannel would tend to dissolve under the current groundwater conditions.

#### *Fluoride, calcium, strontium and barium*

All of the groundwaters tested are considerably undersaturated with respect to halite (Table 4). In contrast, the Wollubar groundwaters appear to be at equilibrium with fluorite (CaF<sub>2</sub>; Figure A3.1), as reflected in the inverse relationship between F and Ca (Figure 8): *i.e.*, for higher Ca concentrations the tendency for fluorite to precipitate will be greater and the F concentration is therefore lower. As dissolved Ca concentrations are about 2 orders of magnitude greater than F, groundwater equilibration will represent a primary control of F concentration only, whereas Ca concentrations may be controlled by equilibration with gypsum (Figure A3.2) for some of the groundwaters at both Wollubar and Golden Hope. Groundwaters are undersaturated with respect to celestine (SrSO<sub>4</sub>; Figure A3.3) and are commonly saturated with respect to barite (BaSO<sub>4</sub>; Figure A3.4). Similar controls on groundwater concentrations of these elements are observed for saline groundwaters at other sites (Gray, 1990, 1991, 1992a,b).

Table 4: SI Values for the Wollubar and Golden Hope groundwaters, for a number of relevant solid phases. (Minimum and maximum values that may represent equilibrium are in bold type)

Mineral	Formula	Wollubar				Golden Hope			
		Min	Max	Mean	Std dev	Min	Max	Mean	Std dev
Calcite	CaCO <sub>3</sub>	-3.9	-1.8	-3.1	0.7	-1.0	<b>-0.2</b>	-0.6	0.4
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	-6.4	-2.5	-4.9	1.4	<b>0.1</b>	<b>0.5</b>	0.2	0.2
Magnesite	MgCO <sub>3</sub>	-3.4	-1.6	-2.6	0.7	<b>-0.2</b>	<b>0.2</b>	0.0	0.2
Halite	NaCl	-2.4	-1.5	-1.9	0.3	-2.5	-2.3	-2.4	0.1
Fluorite	CaF <sub>2</sub>	<b>-0.4</b>	<b>0.4</b>	0.1	0.3	nd	nd	nd	nd
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	-1.1	<b>-0.4</b>	-0.6	0.2	-1.1	<b>-0.2</b>	-0.5	0.5
Celestine	SrSO <sub>4</sub>	-1.2	-0.7	-0.9	0.2	-0.9	-0.6	-0.8	0.1
Barite	BaSO <sub>4</sub>	-0.8	<b>-0.2</b>	-0.4	0.2	-0.9	<b>0.1</b>	-0.2	0.5
Quartz	SiO <sub>2</sub>	<b>0.1</b>	1.3	0.7	0.4	<b>0.2</b>	0.8	0.5	0.3
Amorphous silica	SiO <sub>2</sub>	-1.2	<b>0.0</b>	-0.6	0.4	-1.1	<b>-0.5</b>	-0.8	0.3
Gibbsite	Al(OH) <sub>3</sub>	-2.6	2.6	0.4	1.9	2.0	2.3	2.1	0.2
Amorphous alumina	Al(OH) <sub>3</sub>	-4.9	<b>0.3</b>	-1.9	1.9	<b>-0.3</b>	<b>0.0</b>	-0.1	0.2
Alunite	KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	<b>0</b>	11	6	3	5.3	6.6	5.9	1.0
Jurbanite	AlOHSO <sub>4</sub>	<b>0.1</b>	2.0	0.9	0.4	-1.4	<b>-0.7</b>	-1.0	0.5
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	-3	7	3	3	5.9	6.9	6.4	0.7
Siderite	FeCO <sub>3</sub>	-4.4	-2.0	-3.6	0.8	-1.9	<b>-0.6</b>	-1.4	0.7
Goethite	FeOOH	-1.7	5.1	2.5	2.0	4.5	5.1	4.8	0.3
Ferrihydrite	Fe(OH) <sub>3</sub> ·nH <sub>2</sub> O	-6.7	<b>0.1</b>	-2.5	2.0	<b>-0.5</b>	<b>0.1</b>	-0.2	0.3
Rhodochrosite	MnCO <sub>3</sub>	-3.6	-2.0	-3.0	0.6	-1.8	<b>0.7</b>	-1.4	0.6
Tenorite	Cu(OH) <sub>2</sub> ·H <sub>2</sub> O	-10.7	-4.7	-7.1	1.7	-7.2	-4.7	-5.7	1.3
Smithsonite	ZnCO <sub>3</sub>	-6.4	-4.7	-5.7	0.6	-3.2	-3.2	-3.2	nd
Cerussite	PbCO <sub>3</sub>	-5.4	-3.5	-4.5	0.6	-2.4	-1.3	-1.8	0.6
Theophrasite	Ni(OH) <sub>2</sub>	-10.5	-5.1	-8.0	1.8	-5.6	-4.8	-5.3	0.5
Iodyrite	AgI	-3.2	-2.3	-2.8	0.3	-1.5	-1.5	-1.5	0.0
Sphaerocobaltite	CoCO <sub>3</sub>	-5.5	-3.8	-5.0	0.6	-3.4	-3.4	-3.4	nd
Eskolaite	Cr <sub>2</sub> O <sub>3</sub>	-10	-2	-7	3	2.2	3.3	2.7	0.8
Au Metal	Au	3.7	8.5	6.5	1.7	7.9	7.9	7.9	nd
Uraninite	UO <sub>2</sub>	-11	-3	-7	3	-6.5	-3.3	-4.9	2.2
Rutherfordine	UO <sub>2</sub> CO <sub>3</sub>	-4.2	-2.7	-3.5	0.5	-4.4	-4.2	-4.3	0.1
Na-Autunite	Na <sub>2</sub> (UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub>	-6.7	-1.4	-3.9	1.8	-5.8	-4.7	-5.3	0.8

nd: not determined.

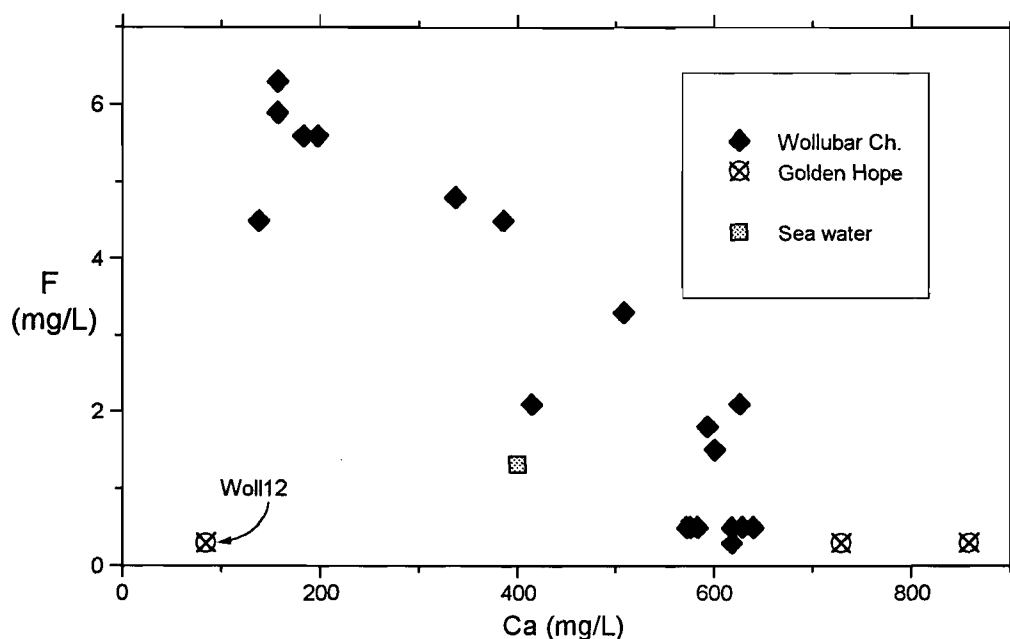


Figure 8: Fluorine vs. Ca for groundwaters from Wollubar palaeochannel and Golden Hope.

#### Potassium and bromine

Data for K and Br (Figures A2.5 and A2.6) suggest that the Wollubar waters occur in two populations:

- (i) one group slightly depleted in K and not depleted in Br;
- (ii) one group highly depleted in K and Br, relative to the sea water line.

By plotting the TDS ratios of these elements vs. pH (Figures 9 and 10), four populations can be distinguished:

- (i) west of the main Boulder-Lefroy shear (relative concentrations near sea water);
- (ii) adjacent to the fault (intermediate concentrations);
- (iii) east of the main shear (strongly depleted in K and Br);
- (iv) Golden Hope (neutral pH, intermediate to high K and Br concentrations).

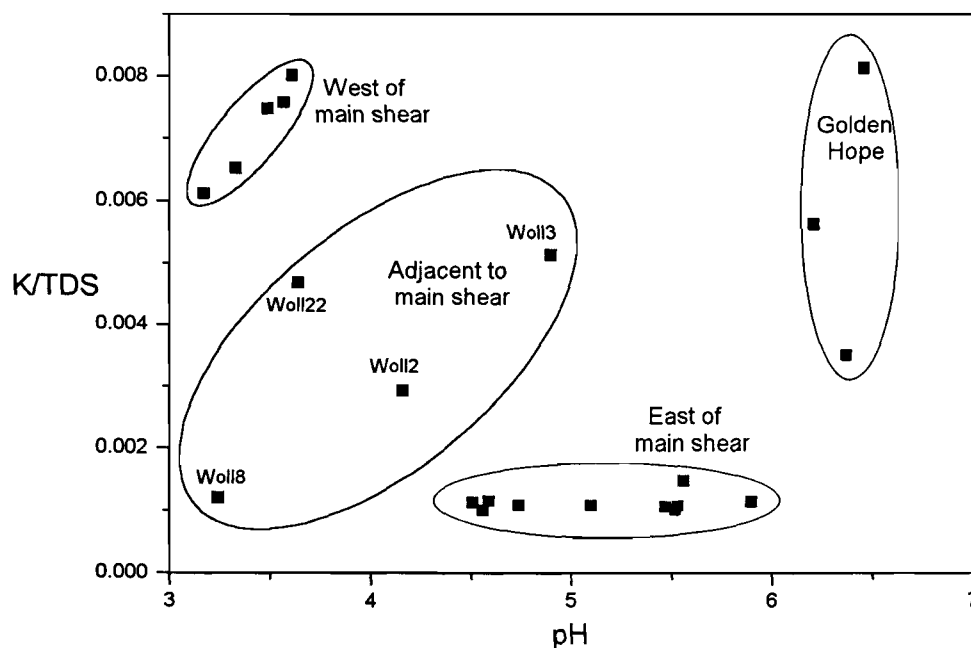


Figure 9: K/TDS vs. pH for Wollubar and Golden Hope groundwaters.



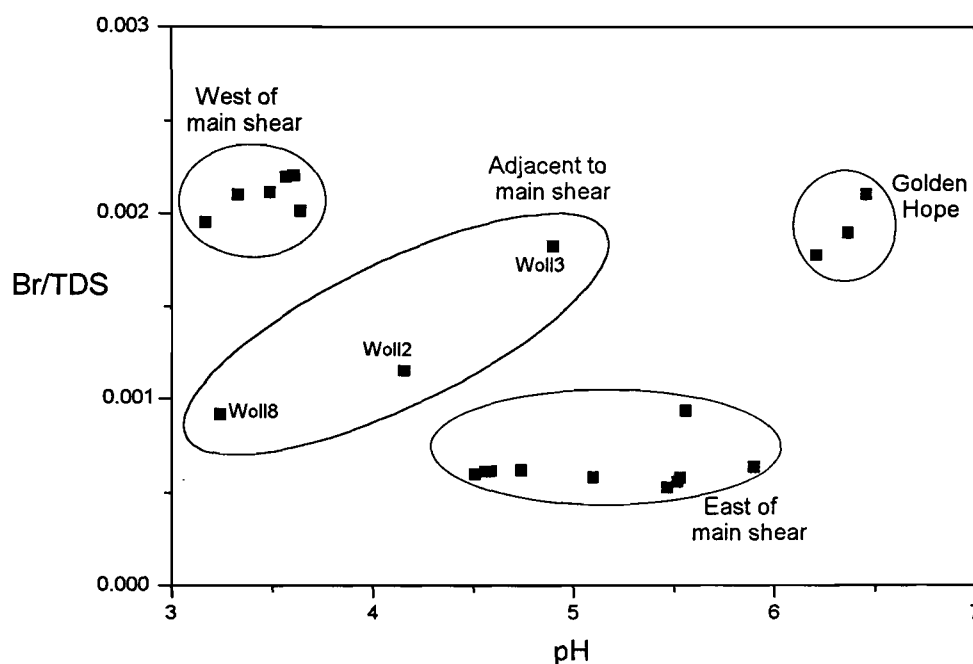


Figure 10: Br/TDS vs. pH for Wollubar and Golden Hope groundwaters.

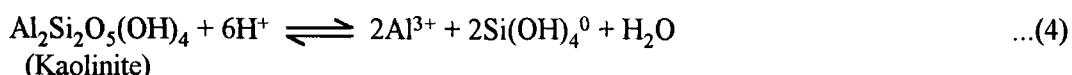
This indicates (at least) two distinct water masses, lying west and east of the shear zone. This correlates with the observation (Section 2.1.3) by Commander *et al.* (1992), based on piezometric measurements, that groundwater derived from Lake Yindarlgooda is flowing back (*i.e.*, southwest; Figure 5) into the Wollubar palaeochannel to discharge to the surface at Wollubar, to flow, ultimately, into Lake Lefroy. Water west of the Boulder-Lefroy shear is flowing eastwards and the area around the shear presumably represents a mixing zone.

#### Aluminium

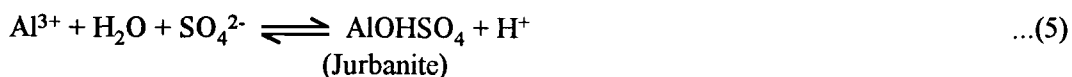
Dissolved Al concentrations significantly increase in acidic conditions, particularly below pH 4 (Figure A2.15). This may reflect groundwater equilibration with specific Al minerals: namely jurbanite ( $\text{AlOHSO}_4$ ) below pH 5 (Figure A3.11) and amorphous alumina [ $\text{Al}(\text{OH})_3$ ] above pH 5 (Figure A3.9). Groundwaters are consistently over-saturated with respect to alunite [ $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ ; Figure A3.10], even though this is the more commonly observed Al-sulphate mineral in acid systems. This equilibration with jurbanite matches results from Panglo (Gray, 1990) and from groundwaters and soil solutions elsewhere (van Breeman, 1973; Karathanasis *et al.*, 1988; Gundersen and Beier, 1988). As discussed in detail in Gray (1990), this suggests that the groundwater equilibrates slowly with alunite and more quickly with jurbanite, allowing the dissolved Al concentrations to be higher than expected if the solution is equilibrated with alunite. Nordstrom (1982) states "that jurbanite provides an approximate upper solubility limit and that alunite provides a lower solubility limit. The lower limit is rarely reached because of slow nucleation and precipitation kinetics."

#### Silicon

The concentrations of dissolved Si in the Wollubar and Golden Hope groundwaters are generally equal or moderately greater than sea water concentration for all samples above pH 4 (Figure A2.16) and are at or slightly above quartz saturation (Figure A3.8). However, in the more acid samples Si concentrations are significantly greater, and reach saturation with amorphous silica. These acid groundwaters are just saturated, or undersaturated with respect to kaolinite (Figure A3.12). Therefore it is postulated that these acid groundwaters are actively dissolving kaolinite:



with the dissolved Al and Si then equilibrating with the phases that have fast precipitation/dissolution reactions, namely jurbanite:



and amorphous silica:



### *Iron*

Dissolved Fe concentrations (Figure A2.20) match other sites. The Wollubar and Golden Hope groundwaters are undersaturated with respect to siderite (Fe<sup>II</sup> carbonate; Figure A3.13), whereas the highly acidic Wollubar waters appear to be at approximate equilibrium with goethite (Figure A3.14), a common Fe<sup>III</sup> oxyhydroxide mineral, and the less acidic Wollubar waters and the Golden Hope waters approach, and in some cases reach, saturation with respect to ferrihydrite (Figure A3.14), a highly soluble Fe<sup>III</sup> oxide.

These observations, and postulated controls, on Al, Si and Fe concentrations very closely match results from Panglo (Gray, 1990), which is the other Yilgarn acid groundwater system that has been extensively studied. This suggests these phenomena to be general for acid groundwater systems in these lithologies.

This described control over Al, Si and Fe solubility is not followed in the case of Woll3, which has a much higher Al concentration than expected at that particular pH (Figure A2.15), reflected in this sample being highly over-saturated with respect to jurbanite (Figure A3.11). Sample Woll3 also has raised concentrations of Si (Figure A2.16), Fe (Figure A2.20) and several minor elements (Section 3.4). These high concentrations presumably reflect highly active weathering in this area, which is very close to the Boulder-Lefroy shear (Figure 5). It therefore appears that there is a clear hydrogeochemical signature of the shear in the groundwater of the palaeochannel.

## **3.4 Minor element chemistry**

### *Speciation analysis*

Most of the minor elements (Table 3) have concentrations similar to those at other sites. The base metal concentrations most closely match those at Panglo, consistent with the hypothesis that similar hydrogeochemical processes are occurring at each site. The minor elements are generally undersaturated with respect to the least soluble mineral phase (Table 4; also see Figures A3.15 - A3.24), indicating little dissolution of these elements and/or that removal from solution via mechanisms such as sorption is occurring. The exception is for groundwaters at Golden Hope, which are oversaturated with respect to eskolaite (Cr<sub>2</sub>O<sub>3</sub>; Figure A3.22).

### *Iodide, phosphate, cesium, barium and molybdenum*

Several elements are enriched in groundwaters at Golden Hope, including I, PO<sub>4</sub>, Cs, Mo and possibly Ba (Figures A2.11 - A2.14, A2.27). Previous results for the Yilgarn (Gray, 1990, 1991, 1992a,b, unpublished data) suggest I, Ba and Mo might be expected to be enriched in groundwaters from mineralized areas, but there are few data for PO<sub>4</sub> and Cs.

#### *Fluorine, scandium, chromium and uranium*

Minor elements that show a specific enrichment in the more acid groundwaters are F, Sc, Cr and U (Figures A2.10, A2.17, A2.18 and A2.50). Scandium and Cr are, like Al, 3+ ions with small ionic radii that form strong bonds with O and OH groups, and are, therefore, expected to have much higher concentrations in acid conditions, whereas U, if present as secondary carbonates or phosphates, would be expected to have a higher concentration in acid conditions. The F enhancement in acid waters is incidental, as F is inversely related to Ca (Figure 8), and Ca concentration is lower in the more acid waters.

#### *Base metals*

The base metals Mn, Co, Ni, Cu, Zn and Pb (Figures A2.19, A2.21 - A2.24 and A2.48) all show much higher concentrations in groundwaters at Wollubar than at Golden Hope but, within the Wollubar sample set, show no clear relationship with acidity. This correlates with results from Panglo, for which there was general enhancement of the base metals in the moderately to highly acid groundwater, but no linear relationship. The only clear interrelationship is between Co and Mn (Figure 11), which show two distinct groups:

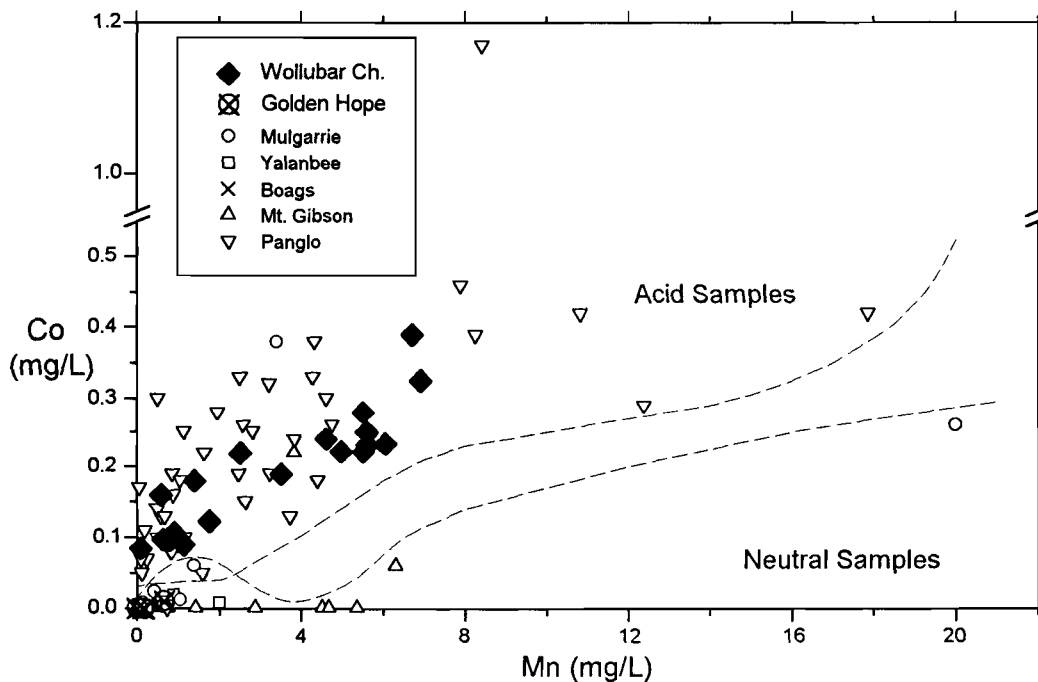


Figure 11: Cobalt vs. Mn for Wollubar palaeochannel and Golden Hope groundwaters.

- (i) acid groundwaters from Wollubar, Panglo, and specific acid samples from Mt. Gibson and Mulgarrie, with a general linear trend between Co and Mn;
- (ii) neutral groundwaters (*i.e.*, Mulgarrie, Mt. Gibson and Boags) for which the range of Mn concentrations is similar to the first group, but Co concentrations are much lower.

This implies differing release mechanisms, observed at a number of sites, under the two regimes: one in neutral conditions releasing Mn but not Co; the second being in acid conditions in which Co and Mn are being released at a ratio of approximately 1:20.

#### *Yttrium and the rare earth elements*

Yttrium and the REE have low concentrations in groundwaters from Golden Hope, but are present in the Wollubar groundwaters at very significant concentrations (Figures A2.26, A2.30 - A2.43). Indeed,

the mean concentrations of La and Ce in the Wollubar groundwaters are greater than those for most of the base metals and are only exceeded by the major elements (Na, Mg, Ca, K, Cl, SO<sub>4</sub>, HCO<sub>3</sub>, Br, Si, Al, Fe and Mn), F and Sr. All other known published data on dissolved REE concentrations are summarized in Table 5. The average REE content of the Wollubar groundwaters is about 5 times that of the highest recorded REE concentrations elsewhere (Carnmenellis metasediment), and the highest REE groundwater at Wollubar (Woll3; Appendix 1) is about 20 times greater. Note, however, that very little data is available for other acid groundwaters in the Yilgarn, so it is possible that this effect may be present elsewhere in the Yilgarn block.

Table 5: Comparative REE concentrations from ground and surface waters

Sample Site		Ref	Dissolved Concentration (µg/L)													
			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Wollubar - mean		1	471	691	92	231	45	12	40	5.5	27	4.9	13	1.8	9.4	1.5
Golden Hope - mean		1	1.0	1.3	0.2	0.7	0.3	0.1	0.3	<0.1	0.2	0.0	0.2	<0.1	0.2	<0.1
Neutral groundwaters (central WA)		2	0.2	0.8	0.2	0.4	0.1	<0.1	0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
Neutral salt lake (southern WA)		2	1.0	0.5	0.2	0.6	0.5	0.3	0.4	0.2	0.6	0.3	0.2	<0.1	0.2	0.1
Groundwaters contacting REE-rich lignites (southern WA)		2	1.3	3.8	0.5	2.3	1.0	0.5	1.0	0.2	0.6	0.3	0.5	0.2	0.5	0.2
Palo Duro basin, Texas - Deep Basin Brine	Sawyer Granite	3	20	40	5.1	27	7.3	2.1	10	1.5		1.4		0.4	1.8	0.25
	" Carbonate		0.9	1.4	0.2	0.6	0.1	0.03	0.1	0.02		0.02		0.01	0.03	0.004
	Friemel Granite		0.2	0.3		0.1	0.02	0.004	0.03	0.003		0.004			0.01	0.001
Carnmenellis, England	Granite	4	2.3	4.6	0.7	2.9	0.7	0.10	0.7		0.5	0.07	0.2		0.2	
	Metasediment		95	8.3	20	69	12	2.4	12		6.3	0.9	2.4		1.2	
Rivers	Amazon	5	0.05	0.1		0.08	0.02	0.005	0.03		0.02		0.01		0.009	0.001
	Connecticut		0.6	0.8		0.4	0.08	0.01	0.07		0.05		0.03		0.03	0.004
Estuarine waters	Amazon	5	0.2	0.5		0.2	0.05	0.01	0.05		0.04		0.02		0.01	0.002
	Connecticut		0.2	0.4		0.2	0.04	0.008	0.03		0.03		0.02		0.006	0.002
Coastal sea waters	Amazon		0.02	0.04		0.02	0.004	0.001	0.006		0.003		0.003		0.004	0.001
	Connecticut	5	0.04	0.06		0.04		0.001	0.010		0.006		0.004		0.004	0.001
Black Sea	Maximum level	6	0.01	0.03		0.01	0.002	0.001	0.003		0.003		0.003		0.002	0.000
Sea water	shallow	7	0.004	0.001		0.002	0.000	0.000	0.001		0.001		0.001		0.001	0.000
	deep		0.007	0.001		0.005	0.001	0.000	0.002		0.002		0.002		0.002	0.000
Buzzard Bay	pore water	8	0.2	0.6		0.2	0.05	0.01	0.05							
Val-les-Bains	Delicieuse	9		0.1		0.1	0.04	0.01	0.06		0.07		0.06		0.08	

References:

1. This study - mean concentrations
2. Gray, unpublished data - mean concentrations
3. Gosselin *et al.* (1992) - high REE samples
4. Smedley (1991) - high REE samples
5. Elderfield *et al.* (1990) - high REE samples
6. German *et al.* (1991) - highest REE sample
7. Piepgras and Jacobsen (1992) - mean concentrations
8. Sholkovitz *et al.* (1989) - highest REE sample
9. Michard *et al.* (1987) - highest REE sample

Based on a recorded abstraction rate of  $2.4 \times 10^9$  L/year for the Wollubar bore field (Commander *et al.*, 1992; results for Northern Borefield, East Location 48 and East Location 51) in 1990, it is calculated that approximately 4000 kg of total REE have been abstracted from the study area (Table 5) over that year. A REE enrichment also occurs in another, nearby, area in the southern part of the eastern goldfields (Gray, unpublished data). At present it is not known whether this enrichment reflects generalized processes for acidic groundwaters in the southern Yilgarn, or whether they are specific for the study area. The general consistency of the data suggests the former, though further sampling of acidic groundwaters would be required to test this hypothesis. However, the high REE abundance along the entire 30 km of the sampled Wollubar palaeodrainage suggests that the high REE concentrations is primarily related to hydrogeochemical rather than lithological effects, and specifically due to the interaction of the solids with highly acid and saline groundwaters.

Table 6: Calculated mean concentrations and total quantities of REE abstracted from the Wollubar bore field in 1990

	Mean Conc. (mg/L)	Abstraction (kg /year)
La	0.47	1143
Ce	0.69	1677
Pr	0.092	224
Nd	0.23	560
Sm	0.045	109
Eu	0.012	29
Gd	0.040	98
Tb	0.0055	13
Dy	0.027	65
Ho	0.0049	12
Er	0.013	31
Tm	0.0018	4
Yb	0.0094	23
Lu	0.0015	4
Total REE	1.4	3990

Chondrite normalized plots for the Wollubar (Figures A4.1 - A4.4) and Golden Hope (Figure A4.5) groundwaters indicate the former to be particularly enriched in the light REE. There are deviations from linearity for Ce for a number of the Wollubar samples. This is commonly observed, due to Ce being present either as the 3+ or the 4+ ion, in comparison with most of the other REE, which are present as the 3+ ion only. The Woll8 and Woll9 samples, which are acidic, but lie outside the palaeochannel and therefore represent groundwaters directly contacting Archaean rocks, are particularly enriched in La (Figure A4.2). This presumably represents a specific lithological effect, whereas the channel samples are an average of inputs from up-gradient, the aquifer sands and the surrounding Archaean rocks.

As observed for the major element data, the samples closest to the shear zone, particularly Woll3, had highly anomalous compositions. Woll3 had enhanced concentrations of Sc, Ga, Y, REE, Pb and U (Figures A2.17, A2.25, A2.26, A2.30 - A2.43, A2.48 and A2.50), whereas Woll2 had a similar, though less intense, enrichment pattern plus anomalous Au and Tl (Figures A2.45 and A2.47) concentrations.



### 3.5 Gold chemistry

The dissolved Au concentrations at Wollubar and Golden Hope are low, relative to other mineralized sites (Figure A2.45). On the basis of previous work (Gray, 1988 and references given therein), the most likely form of dissolved Au at Golden Hope is as the thiosulphate complex  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ , whereas Au present in the Wollubar groundwater, which is acidic, would be expected to be present as the chloride complex ( $\text{AuCl}_2^-$ ). A plot of Au vs. Fe (present in solution as  $\text{Fe}^{2+}$ ) for neutral (*i.e.*, pH of 6 or greater) groundwaters from a number of sites (Figure 12) shows that many samples have significant Au and Fe present in solution. This indicates that in these waters Au is commonly present in a form which will not be reduced, and therefore precipitated, by ferrous ion. The Au thiosulphate complex would show such a lack of effect of  $\text{Fe}^{2+}$  on dissolved Au concentration (Gray, 1988).

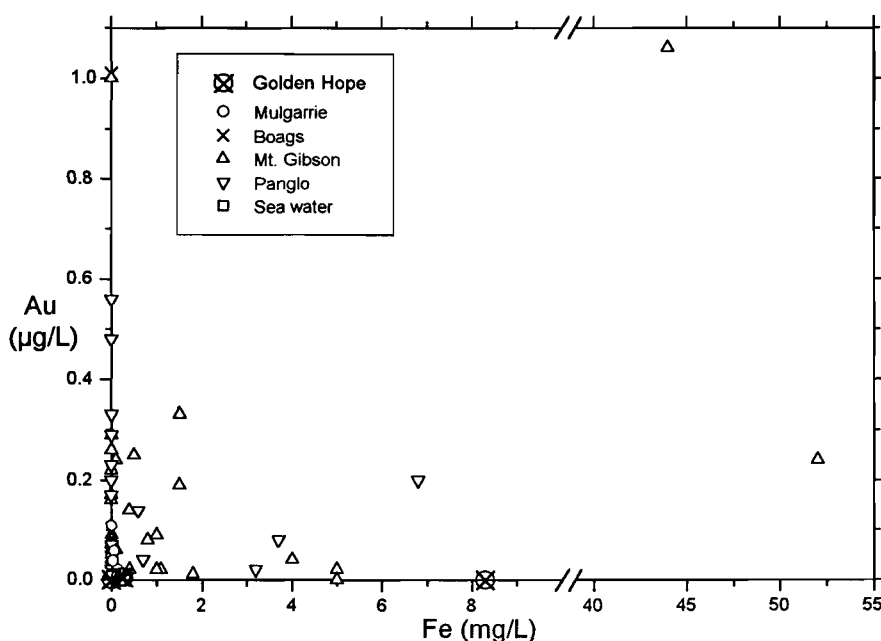
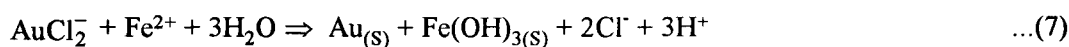


Figure 12: Gold vs. Fe for neutral groundwaters from Golden Hope and other sites.

The thiosulphate ion is released during weathering of sulphide minerals under neutral to alkaline conditions, which appears to match conditions at Golden Hope (Section 3.2). However, dissolved Au concentrations at this site are several orders of magnitude lower than those at other sites where this mechanism is thought to be active. Indeed, Au concentrations are similar to those of sea water (Table 3). The low Au concentrations may reflect retardation of Au dissolution, which may be due to the form of the mineralization, *e.g.*, if Au is protected by quartz veins, it may be inaccessible to groundwaters may not be able to access it. Additionally, as the bore holes were from the periphery of a completed pit, they may therefore not have intersected any significant Au mineralization, thereby explaining the low Au concentration.

For acidic (pH less than 6) groundwaters there is a very strong antipathetic effect of dissolved Fe on Au concentration (Figure 13). This is because ferrous ion will very effectively remove Au chloride from solution:



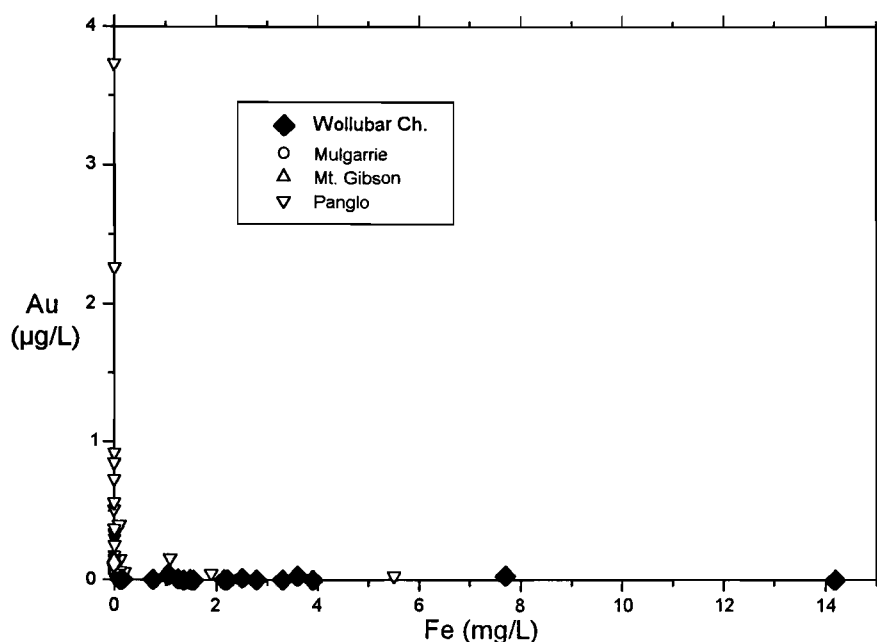


Figure 13: Gold vs. Fe for acid groundwaters from Wollubar palaeochannel and other sites.

The low Au concentration of the Wollubar groundwaters is as expected, *firstly* because many of the samples are Fe-rich and, *secondly*, because the groundwaters are from a palaeochannel system that is mainly underlain by unmineralized areas. However, there are clear enrichments of Au in Woll2 and, to a lesser extent, Woll3 and Woll4 (Figure A2.45; Appendix 1), all of which lie within the mineralized area. Thus, as with the results for the major elements Al, Si and Fe and for many of the other minor elements (Sections 3.3 and 3.4), the palaeochannel waters are reflecting aspects of the basement geology.

Speciation analysis suggests that most of the groundwaters are moderately to highly oversaturated with respect to Au metal (Figure A3.23). This is commonly observed due to the effect of Au-selective ligands even at very low concentrations, and the poor equilibrium between dissolved Au and Au metal at ambient temperatures and pressures (Gray, 1990, 1991).

## 4 MAPPING OF THE DATA

### 4.1 Description of the mapping

Element distribution maps are shown in Appendix 5 and are discussed below. Outlines of the geology and the palaeochannel are included in each plot to facilitate interpretation. Further information on geology or water flow characteristics can be perceived from Figures 1 and 4 and the hole positions and numbers are given in Figure 5.

### 4.2 Total dissolved solids and salinity-related ions

*Total dissolved solids* (Figure A5.1): In terms of TDS, the study area can be divided into two sections: the western part of the channel which has salinities of 6% or less, and the section east of the main shear which has salinities of 9% or more, closely matching results of Commander *et al.* (1992). The salinities are highest in the northern-most samples. Based on the flow model shown in Figure 4 (Section 2.1.3), these saline waters are moving southwards, with a moderate diminishment in salinity due to inflow from other sources. Near the main shear, this groundwater system merges with the less

saline westerly system and then flows southwards. Thus, there are two distinct groundwater systems in the section of the palaeochannel under investigation.

*Magnesium*<sup>1</sup> (Figure A5.2): The eastern part of the drainage has the lowest Mg/TDS ratios, whereas groundwaters at Golden Hope, which intersect or are close to ultramafic rocks, are Mg enriched. There is also a moderate enrichment in those Wollubar groundwaters close to the mineralized area, perhaps reflecting mixing of these "mineralized" waters with groundwater in the major drainage.

*Chloride and sulphate* (Figures A5.3 and A5.4): The eastern part of the drainage is most enriched in Cl and depleted in SO<sub>4</sub>, again supporting the hypothesis that the western and eastern parts of the drainage represent separate groundwater systems.

*Potassium, caesium and bromine* (Figures A5.5 - A5.7): The distributions of these elements are shown as the concentration, rather than the TDS ratio, because, unlike Na, Mg, Cl and SO<sub>4</sub>, they are not correlated to salinity (compare Figures A2.5 and A2.6 with Figures A2.1 - A2.4). The western, less saline, arm of the palaeochannel is richer in K and Br than the eastern, more saline, arm (Section 3.3 and Figures 9 and 10). A similar pattern is observed for Cs (Figure A5.7), except that the Golden Hope samples are particularly anomalous, which is presumably a lithological effect (Figures A2.13 and A5.7).

#### 4.3 Alkaline earth elements

*Calcium* (Figures A5.8 and A5.9): Calcium concentration is only weakly correlated with TDS for the Wollubar groundwaters (Figure A2.7), though there is a broad similarity between the distributions of Ca (Figure A5.8) and TDS (Figure A5.1). When the Ca/TDS ratio is plotted (Figure A5.9), the most Ca-enriched waters occur at and directly east of Golden Hope, possibly representing Ca released during carbonate dissolution (Section 3.3; Eqn. 3).

*Strontium* (Figure A5.10): Strontium and Ca are generally correlated in groundwater (Figure 12). However, unlike Ca, strong groundwater enrichment in Sr is localized to Golden Hope, perhaps because the relatively smaller anomaly (about 2 x background for Sr, compared with about 4 x background for Ca) is swamped by mixing with other groundwaters away from the mineralized area.

*Barium* (Figure A5.11): The Ba distribution is highly variable, with no observed correlation with lithology or groundwater flow. This is probably because Ba concentration is being strongly controlled by equilibration with barite (Section 3.3; Figure A3.4) which, along with kinetic factors such as possible incomplete dissolution or precipitation, could result in the variable distribution.

#### 4.4 Acidity, alkalinity and oxidation potential

*Acidity* (Figure A5.12): The pH distribution shows three different zones along the palaeochannel:

- (i) a very acid (pH 3.2 - 3.6) zone west of the Boulder-Lefroy shear, probably due to the dominant felsic lithologies in this zone (Figure 1), which will have little buffering capacity;
- (ii) a moderately acid (pH 4.2 - 4.9) zone immediately east of the shear, in which there are several tightly folded lithological units;
- (iii) a weakly acid (pH 5.1 - 5.9) zone in the northern part of the study area, which is immediately downstream from ultramafic and basaltic rocks.

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<sup>1</sup> As discussed in Section 3.3, the Mg, Cl and SO<sub>4</sub> data are shown in Figures A5.2 - A5.4 as TDS ratios.

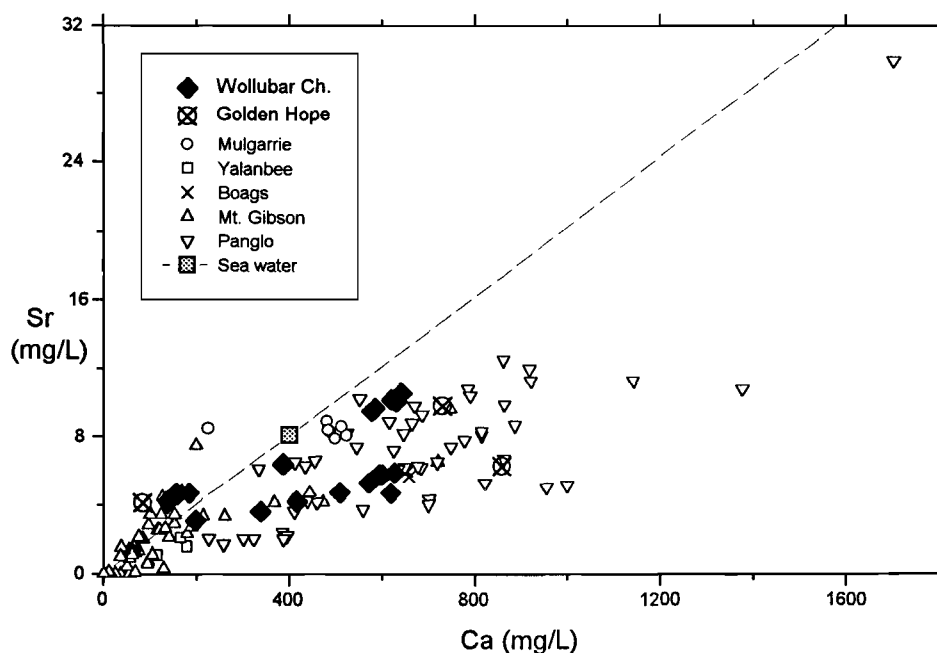


Figure 12: Strontium vs. Ca for groundwaters from Wollubar palaeochannel, Golden Hope and other sites.

The Golden Hope waters are nearly neutral (pH 6.2 - 6.5), consistent with an environment where any acid production is buffered by dissolution of carbonate minerals (Section 3.3).

*Alkalinity* (Figure A5.13): Bicarbonate concentrations are primarily dependant on pH (Figure A2.9), and the  $\text{HCO}_3$  distribution matches this effect. Waters at Golden Hope are particularly rich in  $\text{HCO}_3$  (Section 3.3; Figure A2.9).

*Oxidation potential* (Figure A5.14): The Eh distribution is highly variable. The lowest Eh values are observed at Golden Hope, and the northeast of the Wollubar channel, where the pH values are highest (Figure A5.12). This reflects the broadly inverse relationship between Eh and pH (Figure 6).

#### 4.5 Non-metals

*Fluoride* (Figure A5.15): Fluoride concentration is controlled by fluorite equilibration, and is therefore inversely proportional to dissolved Ca (Section 3.3; Figure 8). Thus, F distribution is the inverse of that of Ca (Figure A5.8).

*Phosphate* (Figure A5.16): Phosphate concentration is below detection for most of the Wollubar samples (Appendix 1), and below sea water concentration for all groundwaters except sample Woll12 at Golden Hope. The highest  $\text{PO}_4$  concentrations are observed at Golden Hope.

*Iodide* (Figure A5.17): Dissolved I is slightly enriched, relative to sea water (Figure A2.11), in the Wollubar channel, and is highly enriched at Golden Hope, consistent with observed I enrichments in mineralized areas at Mulgarrie, Boags, Mount Gibson and Panglo (Gray, 1990, 1991, 1992a,b). Iodide is considered to be a chalcophile element (Fuge and Johnson, 1984, 1986) and is commonly enriched in sulphide environments (Chitayeva *et al.*, 1971).

#### 4.6 Aluminium, gallium and silicon

**Aluminium** (Figures A5.18 and A5.19): Aluminium concentration is primarily related to pH (Section 3.3; Figure A2.15) and this is reflected in the distribution of dissolved Al (Figure A5.18). Speciation calculations indicate that most groundwaters are close to equilibrium with jurbanite, the phase most probably controlling Al concentration at and below pH 5 (Section 3.3). However waters close to the Boulder-Lefroy shear are oversaturated (Figure A5.19), particularly sample Woll3, which has an SI of 1.9, (*i.e.*, oversaturated by at least an order of magnitude). This suggests active weathering at the shear zone, resulting in dissolved Al concentrations well above equilibrium with respect to jurbanite.

**Gallium** (Figures A5.20 and A5.21): Gallium has a similar ionic radius to Al (Ga - 0.62 Å, Al - 0.51 Å) and therefore is almost always found substituted in Al minerals (Goldschmidt, 1954). However, the Ga distribution (Figure A5.20) in the Wollubar and Golden Hope groundwaters matches Al (Figure A5.18) very poorly. A plot of the Ga/Al ratio (Figure A5.21) shows that very few samples have ratios below 0.001, which is the upper limit in most rocks (Gottardi *et al.*, 1978). The ratios at Golden Hope are up to 200 times greater, and many of the Wollubar samples also enriched in Ga. Gallium differs from Al in that it can occur in sulphide minerals, hence the enrichment may reflect the preferential dissolution of sulphides relative to Al-bearing minerals. The Ga/Al may therefore have some value for indicating mineralized and/or sulphide-containing environments.

**Silicon** (Figure A5.22): The highest Si concentrations occur in the western part of the Wollubar palaeodrainage, reflecting the low pH in this area (Figure A5.12). Under these conditions, Si-containing minerals such as kaolinite or feldspar may be dissolving (Eqn. 4), and the Si concentration reaches the level where amorphous Si would precipitate (Section 3.3; Figure A3.8). In the less acid conditions in the eastern part of the palaeodrainage, Si concentrations are close to sea water (3 mg/L).

#### 4.7 First row transition metals

**Chromium** (Figure A5.23): Chromium concentration at Wollubar is primarily related to pH (Section 3.4; Figure A2.18) and the distribution of dissolved Cr closely matches those of pH (Figure A5.12) and Al (Figure A5.18).

**Manganese and cobalt** (Figures A5.24 and A5.25): Manganese concentration is high for all of the Wollubar groundwater samples (Figure A2.19), and is greatest in the eastern part of the palaeodrainage (Figure A5.24), for reasons not understood at present. As discussed previously (Section 3.4; Figure 11), Co distribution (Figure A5.25) closely matches that of Mn.

**Iron** (Figures A5.26 and A5.27): The distribution of Fe is irregular (Figure A5.26), though there appears to be some enrichment close to the main shear. However, concentration can be affected by equilibration with Fe oxides and/or carbonates (Section 3.3; Figures A3.13 and A3.14), which will be sensitive to changes in pH and Eh. The distribution of the SI values for ferrihydrite (Figure A5.27) shows that most groundwaters are moderately to very undersaturated with respect to this mineral, with the exception of the zone at and immediately east of the main shear, which is saturated with respect to this mineral. This suggests that significant concentrations of Fe are being released into solution in this zone, where the Fe concentration is great enough to reach equilibration with ferrihydrite, which is a very soluble phase.

**Nickel, copper and zinc** (Figures A5.28 - A5.30): As discussed previously, these elements are generally enriched in the Wollubar palaeodrainage (Section 3.4; Figures A2.22 - A2.24) and have similar distributions to Mn and Co, with enrichments in the eastern part of the palaeodrainage. None of these elements show enrichment in groundwaters at or near the Boulder-Lefroy shear.

#### 4.8 Scandium, yttrium and the rare earth elements

*Scandium* (Figure A5.31): Scandium is often linked with Y and the REE, though by virtue of its smaller ionic radii (0.75 Å, compared with 0.86 - 1.05 Å for Y and the REE), it is commonly associated with Fe<sup>3+</sup> or Al minerals and has a distinct geochemistry from the REE (Fron del, 1978). The Sc distribution differs markedly to that Fe or Al (Figures A5.18 and A5.26) or the REE (see below), but does appear to show a moderate enrichment at the main shear zone.

*Rare earth elements* (Figures A5.32 - A5.49): There is a major difference between the REE content of the Golden Hope and the Wollubar groundwaters, with the total REE concentrations at Golden Hope being less than 0.01 mg/L, whereas the palaeochannel groundwaters contain between 0.6 and 7 mg/L (Figure A5.32), representing very high REE concentrations. As discussed in Section 3.4 (Figures A4.1 - A4.5), the Wollubar groundwaters are highly enriched in the light REE, relatively to the heavy REE. In addition, the distribution patterns of the light REE (La - Gd; Figures A5.33 - A5.39) differ significantly from those of the heavy REE (Tb - Lu; Figures A5.40 - A5.46):

- (i) the light REE are strongly enriched in the immediate region of the main shear, and are also moderately enriched in the western part of the palaeodrainage, with relatively low concentrations in the northeast part of the study area;
- (ii) the heavy REE tend to have a general enrichment at, and to the east of, the main Boulder-Lefroy shear, with the west and northeast having similar, moderately anomalous, concentrations.

These phenomena can also be demonstrated by looking at some of the standard REE ratios (Taylor and McLennan, 1985):

$$\begin{aligned} & \text{La}_n / \text{Yb}_n \\ & \text{Ce} / \text{Ce}^* = 2 \text{Ce}_n / (\text{La}_n + \text{Pr}_n) \\ & \text{Eu} / \text{Eu}^* = \text{Eu}_n / ((\text{Sm}_n \text{Gd}_n)^{0.5}) \end{aligned}$$

where  $\text{La}_n$  (for example) denotes the Chondrite normalized La concentration.

Thus, the most La enriched (relative to Yb) samples occur for the acid samples lying between Golden Hope and the palaeochannel (Figure A5.47), whereas the samples for the east part of the channel tend to have the least La enrichment. There are some Ce/Ce\* ratios well below 1, particularly for the samples lying east of Golden Hope (Figure A5.48), indicating major Ce depletion, relative to Chondrite. Cerium depletion occurs as a result of the lower solubility of Ce in oxidizing conditions, due to its tendency to form the less soluble Ce<sup>4+</sup> ion (Hoyle *et al.*, 1984), unlike the other REE, which have the 3+ charge. Such oxidizing conditions are possibly occurring in this Ce depleted zone. Europium may also be anomalous, due to the formation of the soluble Eu<sup>2+</sup> ion under reducing conditions. Most of the Wollubar samples are depleted in Eu (Figure A5.49), suggesting that earlier reducing conditions may have resulted in a relative loss of Eu from the sediments. Exceptions to this are waters at Golden Hope and at Woll3, which have normal or positively anomalous Eu/Eu\* ratios. This may reflect direct influence from weathering of the underlying Archaean rocks.

*Yttrium* (Figure A5.50): The ionic radii of Y (0.90 Å) most closely matches those of Ho (0.91 Å) and Er (0.89 Å), and the Y distribution (Figure A5.50) is similar to the distributions of these two elements (Figures A5.42 and A5.43), suggesting Y to be behaving as a REE, with ionic radius to be the major controlling factor.

#### 4.9 Second and third row transition elements, metalloids and lead

*Molybdenum and tungsten* (Figures A5.51 and A5.52): Molybdenum and W can occur in sulphides (Evans *et al.*, 1978; Evans and Krauskopf, 1978). The high concentrations of these elements in groundwaters from Golden Hope and in the palaeochannel adjacent to the main shear zone possibly reflect dissolution of these elements during weathering of sulphide minerals.

*Silver and gold* (Figures A5.53 and A5.54): Both these elements appear to be enriched in the Wollubar groundwaters close to the main Boulder-Lefroy shear. However Au differs from Mo, W and Ag in that it is not enriched at Golden Hope (Figure A5.54). The reason for this is not clear, but may be due to samples being distant from the main mineralization (Section 3.5).

*Cadmium and mercury* (Figures A5.55 and A5.56): Cadmium concentrations are close to the detection limit, and show no clear distribution pattern (Figure A5.55). Cadmium tends to be associated with Zn (Brehler, 1978), though the distribution patterns of Cd and Zn (Figure A5.30) differ, perhaps suggesting a combination of factors affecting dissolved Cd concentrations. Mercury, like many of the other second and third row transition elements, is strongly enriched in groundwaters from Golden Hope and adjacent to the main shear (Figure A5.56).

*Thallium* (Figure A5.57): Like a number of the second and third row transition elements, dissolved Tl concentration tends to be greatest at Golden Hope and in the palaeochannel close to the main shear, presumably because of its tendency to be present in sulphide phases (Sahl *et al.*, 1978a).

*Tin and lead* (Figures A5.58 and A5.59): The Sn distribution (Figure A5.58) is highly variable, and shows no enhancement close to the main Boulder-Lefroy shear. This is possibly because Sn is present in oxide phases such as cassiterite ( $\text{SnO}_2$ ), the most common Sn mineral (Bergerhoff *et al.*, 1978), rather than as a sulphide. Lead, however, is commonly present as galena ( $\text{PbS}$ ; Sahl *et al.*, 1978b) and, like the other chalcophile elements, is enriched in the palaeodrainage close to the main shear (Figure A5.59). Like Au (Figure A5.54), it does not appear to be enriched in the Golden Hope groundwaters.

#### 4.10 Actinide elements

*Thorium* (Figure A5.60): Dissolved Th concentrations are low, consistent with the generally insoluble nature of the  $\text{Th}^{4+}$  ion and its association with minor resistate phases.

*Uranium* (Figures A5.61 and A5.62): The U concentration is greatest in the acid groundwaters to the west of the main shear (Figure A5.61), as would be expected if U were present as secondary carbonate, phosphate or vanadate minerals. When the sample SI values for Na-autunite [ $\text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2$ ; chosen as representative of secondary U phosphates or vanadates] are plotted to remove this pH effect (Figure A5.62), the groundwaters to the east are closer to saturation (though still undersaturated by 3 to 4 orders of magnitude). Sample Woll3 is again anomalous, with the highest SI value.

#### 4.11 General distribution patterns

Most of the elements analysed in the Wollubar and Golden Hope groundwaters can be grouped into specific groups, based on their concentration distribution:

- (i) major elements, indicating hydrological differences between the western and eastern sections of the palaeodrainage (TDS, Cl,  $\text{SO}_4$ , K, Cs, Br);
- (ii) transition metals, principally enriched in the eastern part of the palaeodrainage (Mn, Co, Ni, Cu);
- (iii) elements whose concentration is primarily controlled by pH (Al, Si, Cr, U);

- (iv) elements enriched in the Golden Hope groundwaters and at the intersection of the Wollubar palaeodrainage with the main Boulder-Lefroy shear (Ga, Fe, Mo, W, Ag, Hg, Tl);
- (v) elements primarily enriched at Golden Hope (Mg, SO<sub>4</sub>, Cs, Ca, Sr, HCO<sub>3</sub>, PO<sub>4</sub>, I);
- (vi) elements primarily enriched at the intersection of the Wollubar palaeodrainage with the main Boulder-Lefroy shear (Sc, Y, REE, Au, Pb).

Additionally, elements such as Al, Si and U, which are highly enriched in acid conditions, have significantly greater concentrations in the palaeodrainage samples near the main shear than would be expected at the observed pH.

The Boulder-Lefroy shear is the principal host for Au mineralization, and the hydrogeochemistry of groundwater close to this shear zone is thus expected to have a "mineralized" signature, as is observed. However, although some elements are enriched both at Golden Hope and in the channel groundwater near the shear (group iv), there are major differences in other elements enriched at Golden Hope (group v) compared to the channel near the shear (group vi). These differences may be primarily due to pH effects. Those elements enriched in both systems appear to be those associated with sulphides, whereas most of the elements enriched at Golden Hope alone are probably carbonate associated. It is postulated (Section 3.3) that Golden Hope represents an area where acid production during sulphide mineralization is being buffered by dissolution of carbonates. The high concentrations of Cs, PO<sub>4</sub> and I at Golden Hope alone suggest that these elements are also present in carbonates or other phases that are readily dissolved. The elemental anomaly described here, and the hypothesized origin, is very similar to results for the Boags deposit (Gray, 1992a) and areas at Mt. Gibson (Gray, 1991).

In the channel, by comparison, all carbonates have been dissolved during the continuous flow of acidic groundwater so that the "carbonate" signature is not observed. Elements specifically enriched where the acid palaeochannel groundwaters pass over the main shear zone include Sc, Y, REE, Au, Pb and (relative to the expected concentration at the observed pH) Al, Si and U. This could reflect a different mineralogical suite to the Golden Hope area, but is more likely to represent acid weathering of similarly mineralized material. More difficult to explain is why Au is observed in the palaeochannel groundwater (presumably present as Au chloride; Section 3.5), but not at Golden Hope, unlike other analogous areas such as Boags and Mt. Gibson, which had highly enhanced Au concentrations.

## 5 DISCUSSION

The results described in this Report relate to two different areas of interest: Golden Hope, which add to a database on ore body groundwaters, and the Wollubar palaeodrainage groundwaters, which represent an acid groundwater system overlying mineralized Archaean rocks along part of its flow path. These two areas are discussed separately.

### 5.1 Golden Hope groundwaters

The Golden Hope groundwaters are very similar to deep waters from Boags (Gray, 1992a) and from the Hornet pit at Mt. Gibson (Gray, 1991), with characteristics in common including:

- (i) near neutral pH and relatively low Eh (Section 3.2);
- (ii) groundwater enrichments in Fe, SO<sub>4</sub> (possibly from sulphides) and HCO<sub>3</sub>, Mg and, to a lesser extent, Ca and Sr (possibly from carbonates), probably reflecting oxidation of sulphide minerals at depth, with neutral pH conditions being maintained via dissolution of carbonates (Section 3.3);



- (iii) groundwater enrichments in a number of "pathfinder" elements, which at Golden Hope includes PO<sub>4</sub>, Ga, Mo, Ag, I, Cs, W, Hg and Tl, many of which are commonly associated with sulphides.

The Golden Hope groundwaters are different from those at Boags and Mt. Gibson in that they are not Au-rich. This parallels results for a limited hydrogeochemical survey at Mulgarrie, where a single sample intersecting mineralization was enriched in a number of pathfinder elements but not in Au (Gray, 1992b). The reasons for such a difference are not clear, because in all known respects the Golden Hope groundwaters should be just as effective in dissolving Au as the thiosulphate complex (Sections 3.3 and 3.5) as the other sites investigated. If dissolved Au is to be used as an exploration tool it is critical to understand why strong Au enrichments are only occurring at some sites.

In addition to Au, the pathfinder elements listed above (possibly with As, which was not analysed for at this site) may also have value for exploration. Most of these elements appear to be sulphide associated, so they may not be directly related to Au. However, a system for easily pinpointing sulphide enrichments may still have exploration value.

## **5.2 Wollubar palaeochannel groundwaters**

In general, results for Wollubar closely matched observations at other sites with acid groundwaters. This suggests that some general assumptions on dissolved metal abundances, as detailed in this report, can be made and variations (*e.g.*, in Co/Mn or Ga/Al ratios) may have specific lithological or exploration significance. The groundwater results for the Wollubar palaeodrainage are encouraging in terms of the exploration potential of such acid systems, in a manner analogous to acid groundwaters in direct contact with mineralization, as at Panglo (Gray, 1990). Close to the Boulder-Lefroy shear, which is the major host for Au mineralization, groundwater samples were enriched in the sulphide-associated elements Ga, Fe, Mo, W, Ag, Hg, Tl and possibly Ga (in common with the Golden Hope system), the acid-soluble elements Sc, Y, REE, and (relative to the expected concentration at the sample pH) Al, Si and U, with additional enhancements in Pb and Au. Therefore, even though these Wollubar samples represent a high volume aquifer, with most of the groundwater flow occurring through the Wollubar Sandstone, there is still a multi-element signal in groundwater close to the main shear.

This area may well be especially favourable for the presence of a distinct signature of mineralization in the palaeochannel groundwater, because mineralization is associated with a major shear. Such a shear will tend to be actively weathering (Gray, unpublished data) and could be highly permeable, leading to greater water flow into the overlying palaeodrainage. Further studies in areas where acid palaeodrainages overlie mineralization not associated with major shears would presumably clarify the importance of geological structures for such geochemical signatures in the groundwater. In contrast, neutral palaeodrainage systems would be expected to have very different hydrogeochemistries to acid systems. Work at Mulgarrie (Gray, 1992b) and near Laverton (Gray, unpublished data) suggests that neutral groundwaters in overburden or barren weathered rocks overlying mineralization have very low dissolved Au concentrations. However, in both cases there was no major permeable aquifer, so there may have been hydrological barriers to groundwater enhancements such as those observed at Wollubar. Again, further work where there are neutral groundwaters flowing through an extensive aquifer such as the Wollubar Sandstone would be of value in further elucidating the potential of such groundwater systems for exploration.

## 6 SUMMARY

The hydrogeochemistries of groundwaters associated with the Golden Hope ore body and the Wollubar palaeodrainage were investigated. The Golden Hope groundwaters match previous results for deep mineralized groundwaters, with neutral pH, low to moderate Eh, and anomalous Fe, SO<sub>4</sub> (from sulphides), Mg, Ca, Sr and HCO<sub>3</sub> (from carbonates). These data, and speciation results indicating groundwater equilibration with calcite, dolomite and magnesite, suggests that sulphides are dissolving at the weathering front, with the resultant acidity being neutralized by carbonate dissolution. Other minerals that appear to be in equilibrium with some or all of the Golden Hope groundwaters are gypsum, barite, amorphous alumina and ferrihydrite. In addition, the Golden Hope groundwaters are enriched in Ga, Mo, W, Ag, Hg, Tl and I, which are commonly associated with sulphides, and in PO<sub>4</sub> and Cs.

Total salinity, K and Br data indicate that the palaeochannel groundwaters to the west and to the east of the main Boulder-Lefroy shear are hydrochemically distinct, consistent with the proposal by Commander *et al.* (1992) that the two systems flow into each other near the region of the shear and then flow south into Lake Lefroy. The palaeodrainage system is acid, with pH varying from near 6 at the northern part of the study area down to 3 in the western arm. The Wollubar groundwaters differ from some other acid systems in that they were Fe-rich, and therefore tend to have lower Eh values. The mineral phases that appear to be equilibrating with some or all of the groundwaters, and the elements whose concentrations are being controlled are:

- (i) fluorite (F);
- (ii) gypsum (Ca);
- (iii) barite (Ba);
- (iv) amorphous silica, for pH < 4 (Si);
- (v) jurbanite, for pH < 5 (Al);
- (vi) amorphous alumina, for pH > 5 (Al);
- (vii) ferrihydrite, for pH > 4.5 (Fe);

In general, results for Wollubar closely match observations at other sites with acid groundwaters. With the exception of Au, for which speciation analysis works poorly, the other minor elements are undersaturated with respect to their least soluble mineral phase, indicating that dissolution has occurred slowly or that concentration is being limited by other mechanisms such as sorption on, or co-precipitation with, Fe oxides. With the exception of the higher charge ions Sc, Cr and U, most metals, and particularly the base metals, showed no clear relationship with pH, possibly because their abundance is also affected by other hydrogeochemical or lithological factors. The concentration of the REE is very high at Wollubar, both in the palaeodrainage and where acid waters are directly contacting Archaean material, being at least 5 times greater than any other known groundwater abundances, possibly due to the highly acid and saline conditions.

The palaeodrainage samples adjacent to the main Boulder-Lefroy shear showed particularly anomalous characteristics, being enriched in a similar "sulphide suite" as for the Golden Hope samples (Ga, Fe, Mo, W, Ag, Hg and Tl), in acid soluble elements (Sc, Y, REE and, relative to the observed pH, Al, Si and U) and also Au and Pb. This may represent acid weathering of a similar mineralized material to that at Golden Hope, and indicates that even palaeochannel groundwaters having a high flow rate can have solution characteristics relating to underlying mineralization.

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