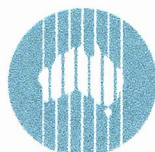




CRCLEME

Cooperative Research Centre for
Landscape Evolution & Mineral Exploration



CSIRO
EXPLORATION
AND MINING



Australian Mineral Industries Research Association Limited ACN 004 448 266



**OPEN FILE
REPORT
SERIES**

INVESTIGATION OF THE HYDROGEOCHEMICAL DISPERSION OF GOLD AND OTHER ELEMENTS FROM MINERALIZED ZONES AT THE GRANNY SMITH GOLD DEPOSIT, WESTERN AUSTRALIA

Volume I

D.J. Gray

CRC LEME OPEN FILE REPORT 93

March 2001

(CSIRO Division of Exploration and Mining Report 383R, 1993.
2nd Impression 2001.)

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



INVESTIGATION OF THE HYDROGEOCHEMICAL DISPERSION OF GOLD AND OTHER ELEMENTS FROM MINERALIZED ZONES AT THE GRANNY SMITH GOLD DEPOSIT, WESTERN AUSTRALIA

Volume 1

D.J. Gray

CRC LEME OPEN FILE REPORT 93

March 2001

(CSIRO Division of Exploration and Mining Report 383R, 1993.
2nd Impression 2001.)

© CSIRO 1993

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

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

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

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

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

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

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

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

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

P241A: Gold and associated elements in the regolith - dispersion processes and implications for exploration (1991-1993). Leader: Dr C.R.M. Butt.

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

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

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

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

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

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

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

Although the confidentiality periods of Projects P252 and P409 expired in 1994 and 1998, respectively, the reports have not been released previously. CRC LEME acknowledges the Australian Mineral Industries Research Association and CSIRO Division of Exploration and Mining for authority to publish these reports. It is intended that publication of the reports will be a substantial additional factor in transferring technology to aid the Australian mineral industry.

This report (CRC LEME Open File Report 93) is a second impression (second printing) of CSIRO, Division of Exploration Geoscience Restricted Report 383R, first issued in 1993, which formed part of the CSIRO/AMIRA Project P409.

Copies of this publication can be obtained from:

The Publication Officer, c/- CRC LEME, CSIRO Exploration and Mining, Private Bag 5, Wembley, WA 6913, Australia. Information on other publications in this series may be obtained from the above or from <http://leme.anu.edu.au/>

Cataloguing-in-Publication:

Gray, D.J.

Investigation of the hydrogeochemical dispersion of gold and other elements from mineralised zones at the Granny Smith Gold Deposit, Western Australia.

ISBN v1: 0 643 06685 3 v2: 0 643 06686 1 set: 0643 066888 8

1. Regolith - Western Australia - Yilgarn Block 2. Gold ores - Western Australia - Yilgarn Block 3. Geochemistry - Western Australia - Yilgarn Block 4. Geology - Western Australia - Yilgarn Block

I. Title

CRC LEME Open File Report 93.

ISSN 1329-4768

PREFACE

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

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

The Granny Smith gold deposit is in an area where few groundwater studies have been conducted, with several Au deposits, located in residual areas and beneath transported sediments. The investigation was designed to evaluate the potential of hydrogeochemical exploration in this environment and to provide guidelines for the sampling, analysis and interpretation of the data. The groundwaters are neutral with variable salinity and provide a further comparison with the acid / saline groundwaters of the southern Yilgarn Craton. Unfortunately, it was not possible to obtain good background samples, with the results obtained suggesting that dissolved Au is a poor indicator of mineralization at this site, though other pathfinder elements could have potential for Au exploration.

C.R.M. Butt and R.E. Smith,
Project Leaders.
April, 1995

ABSTRACT

The hydrogeochemistry, and in particular, the usefulness of groundwater as an exploration medium, has been tested at the Granny Smith gold deposit. Two different sample treatment methods were used and compared:

- (i) no field treatment - samples filtered and acidified in the laboratory about 10 days later;
- (ii) samples filtered and acidified in the field.

The latter procedure is most commonly followed in groundwater investigations. Comparisons of the results indicated that agreement between the two methods was generally good, except for Fe, Al and, to a lesser extent, Au. However, given the importance of these elements in exploration and for understanding hydrogeochemical processes, it is recommended that the latter method be used.

Groundwaters at Granny Smith are generally neutral, with variable salinity. The waters appear to be depleted in Mg, K and Br, suggesting that halite (NaCl) is dissolving in the groundwater and displacing these ions. Additionally, there is a minor enrichment in Ca and SO_4 in the less saline samples, which is possibly due to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) dissolution.

Although the hydrogeochemistry of the minor elements at Granny Smith is similar to that of other Yilgarn sites, dissolved Au concentrations at Granny Smith are very low and, indeed, are not much higher than sea water. The reasons for this are not understood, but the potential for dissolved Au alone as an exploration tool in this area is predicted to be poor.

One additional problem at this site is that the groundwater system appears to be highly stratified. Samples obtained via dewatering bores appear to be representative of a deep saline system, whereas those obtained using a bailing system appear to be sampling more shallow, fresher, groundwater. At Windich, mineralization occurs at depth, and the water samples, which were all obtained by bailer, do not appear to be from groundwater contacting mineralization. This may explain why the dissolved Au concentrations in the Windich groundwater samples are very low.

At the Goanna and Granny pits, the water samples are obtained from the dewatering bores, and appear to be in contact with primary Au mineralization. Samples in areas of high Au grade are enriched in Au (relative to Windich), As, Co, Mn, Mo, Ni, Pb, Sb, Tl and Zn, presumably reflecting the geochemistry of the Au mineralization. Arsenic, Mo, Sb and Tl are commonly associated with Au mineralization, whereas Pb and Zn enrichments may reflect associated galena (PbS) and sphalerite (ZnS), and Mn, Co and Ni have been observed to be enriched in mineralized groundwaters at other sites. Thus, this multi-element association may offer scope for exploration.

There is also some potential for elements which may be associated with mineralization, but which are soluble and tend to be readily dispersed, as a regional groundwater exploration tool. These possibly include As, I and Cs. However, further sampling distant from mineralization would be required to test this possibility.

The generally low Au concentrations in all of the groundwater samples, and the major inconsistency between results for Goanna and Granny and those for Windich, suggest that hydrogeochemistry would not be a very useful exploration method in this area. However, the reasons for these effects are only partially understood. Further work in similar, though hopefully less disturbed areas, may be of value in fully understanding the hydrogeochemistry of such deposits.

TABLE OF CONTENTS

1	INTRODUCTION	1
2	SITE STUDY AND METHODS	2
2.1	Site characteristics	2
2.2	Sample collection, treatment and analysis	2
2.3	Speciation analysis	6
3	RESULTS	7
3.1	Comparison of analyses	7
3.2	Comparison of the two sample treatments	7
3.3	Chemistry of Granny Smith groundwaters	8
3.3.1	Comparison with results from other Yilgarn waters.	8
3.3.2	Acidity and oxidation potential	8
3.3.3	Major ion chemistry	11
3.3.4	Minor element chemistry	12
3.3.5	Gold chemistry	13
4	MAPPING OF THE DATA	14
4.1	Description of the mapping	14
4.2	Salinity, pH and Eh	14
4.3	Major elements and ions	14
4.4	Minor elements	15
4.5	General distribution patterns	16
5	DISCUSSION	18
6	SUMMARY AND CONCLUSIONS	18
	ACKNOWLEDGMENTS	19
	REFERENCES	20

1 INTRODUCTION

Recent work in Australia and elsewhere (Morris, 1982; Hamilton *et al.*, 1983; Giblin and Snelling, 1984; Runnells, 1984; Dissanayake and Weerasooriya, 1986; Hall *et al.*, 1986; McHugh, 1988; Bergeron and Choinière, 1989; Dekkers *et al.*, 1989; Cidu and Edmunds, 1990) has suggested that hydrogeochemistry may be useful for exploration for Au and other metals. A primary justification given is that groundwater anomalies may be broader and more regular than the mineralization and secondary dispersion halo, thus enhancing the exploration signature. In addition, areas of high reactivity (*e.g.*, faults and shear zones) may have distinct hydrogeochemical signatures even where they are unremarkable in terms of elemental abundances, and where normal drilling makes petrographic study difficult. However, such effects may also be counter-productive, as interpretation may become complicated. Hydrogeochemical studies may also expand information on how various materials are weathering, which may enhance understanding of saprolite geochemistry. This may benefit in the development of weathering and geochemical models, which are essential for effective exploration in regolith dominated terrain.

The aims of the project are:

- (i) to provide information on whether groundwater can be used successfully as an exploration medium at the Granny Smith gold deposit, and if so, how it could be done most effectively and economically;
- (ii) to determine whether secondary Au deposits might be expected in the vicinity;
- (iii) to yield data on geochemical dispersion processes;
- (iv) to contribute to a groundwater database on the characteristics of groundwaters at various sites, and to enhance our understanding of groundwater processes in mineralized zones.

The Granny Smith gold deposit holds considerable interest for hydrogeochemical investigations for a number of reasons:

- (i) it lies north of the Menzies line, in the eastern Yilgarn, in an area of extensive hardpan, and represents an area for which there have been few groundwater investigations;
- (ii) the mineralization passes through major changes in groundwater salinity, enabling study of the effect of salinity changes on the chemistry of Au and other elements;
- (iii) groundwater investigations may be complementary to other studies conducted by CSIRO at this site: namely geochemical and mineralogical investigations of the hardpan (Lintern and Butt, 1993). It is considered that groundwater studies are most useful when combined with other geochemical studies.

The scope of this study includes a comparison of differing field sample treatments, the influence of changes in salinity 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 sites.

2 SITE STUDY AND METHODS

2.1 Site characteristics

The Granny Smith Au deposit is 25 km south of Laverton at latitude 28°48'S, longitude 122°25'E (Figure 1)¹. The geology of the deposit is described in detail in Hall and Holyland (1990), and is briefly discussed below. The sample area includes Goanna and Granny pits, with a further pit planned at Windich (Figure 1) at the time of sampling. Near the Windich ore zone, the local geological sequence is characterized by thick medium to fine grained, massive siltstone and shale, capped by BIF and subordinate tuff (Figure 2). To the north and east, in the intermediate area of the Granny ore zone, the sequence consists of more than 100 m of quartz-rich greywacke and lithic wacke. There are minor shale interbeds and sandstones, with a possible basal conglomerate with clasts of shale, quartz, quartzite, BIF and feldsparphyric volcanics. At the Goanna ore zone, the sequence is similar, though with a higher component of BIF (Figure 2) in the hanging wall sequence, and a lack of conglomerate.

A diorite-granodiorite intrusion crops out to the west of the Granny Smith deposit (Figure 2), and underlies sediments over much of the area. The eastern contact with overlying sediments is the locus of mineralization at the Granny ore zone (Figure 1) and the diorite hosts mineralization at Windich. Mineralization is continuous over at least 3500 m, and is more intensely developed at the Goanna, Granny and Windich ore zones (Figure 1). At Goanna, the shear zone and mineralization are entirely hosted in oxidized and weathered metasediments. BIF is prominent and mineralized in the hanging wall, but absent in the footwall. The Granny zone is located 1500 m south, where the shear zone forms the contact between the diorite-granodiorite intrusive and the overlying sediments (Figure 2). Windich occurs a further 800 m south, on the southeastern corner of the intrusive-sediment contact. The mineralization is non-outcropping, occurring in granodiorite and sediments.

Gold is significantly depleted from the upper 20 m of the weathering profile, but there is little evidence of widespread supergene enrichment. The Granny ore zone is located mostly in the regolith, which is 50 to 80 m thick. The profile is deeper adjacent to the mineralized contact and along the shear zone to the north (Figure 1). At Goanna, the mineralized zone is strongly weathered to at least 70 m, whereas at Windich the mineralization occurs at and above the fresh rock - oxidized rock boundary.

Elevation of the study area declines southwards from a hill north of Goanna, with another significant rise 100 m south of Windich. Prior to the building of a retaining wall, the major drainage flowed south, to the east of the ore zones, before turning southwest between Granny and Windich (Figure 1). Groundwaters sampled during drilling varied from 1% total dissolved solids (TDS) at the northern end of the study area to about 20% TDS at Windich (S. Hunt, verbal communication 1992).

2.2 Sample collection, treatment and analysis

Sampling was done in late 1992. Five water samples from Goanna and Granny Smith were taken by sampling dewatering bores, and 12 samples at Windich and 2 samples north of Goanna were bailed from bore holes using a pump-sampler (Table 1; Figure 2). Two different sample treatments were used at each site:

- (i) one sample collected without any field treatment, and stored in an air-tight bottle, without air pockets. Filtering and acidification was then done in the laboratory about 10 days later, followed by analysis. While this procedure may be adequate for exploration purposes, such

¹ Note that, for simplicity, 6812500 mN (for example) is denoted as 12500 mN and 443000 mE (for example) is denoted as 3000 mE in all discussion and figures.

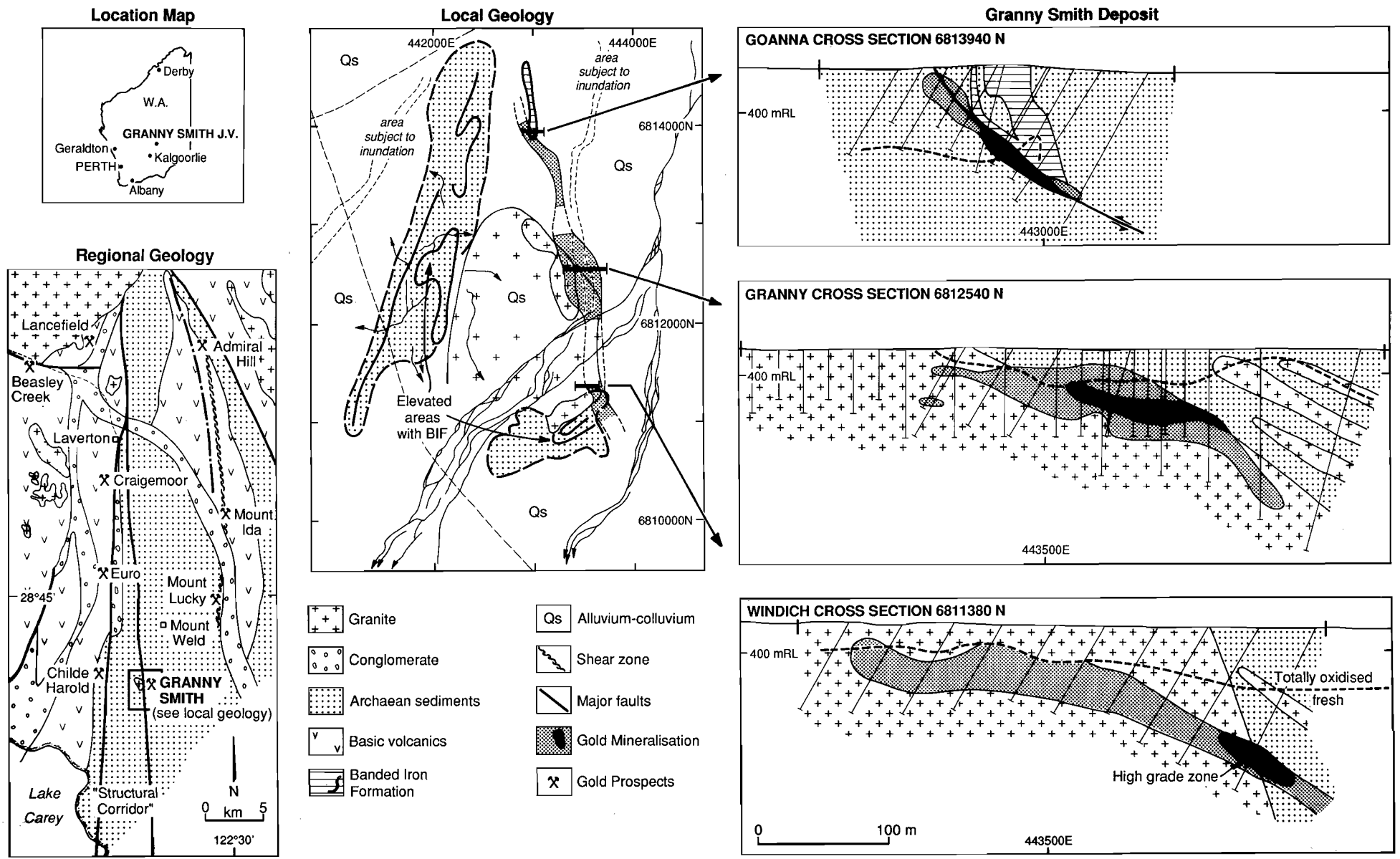


Figure 1: Geology of the Granny Smith gold deposit

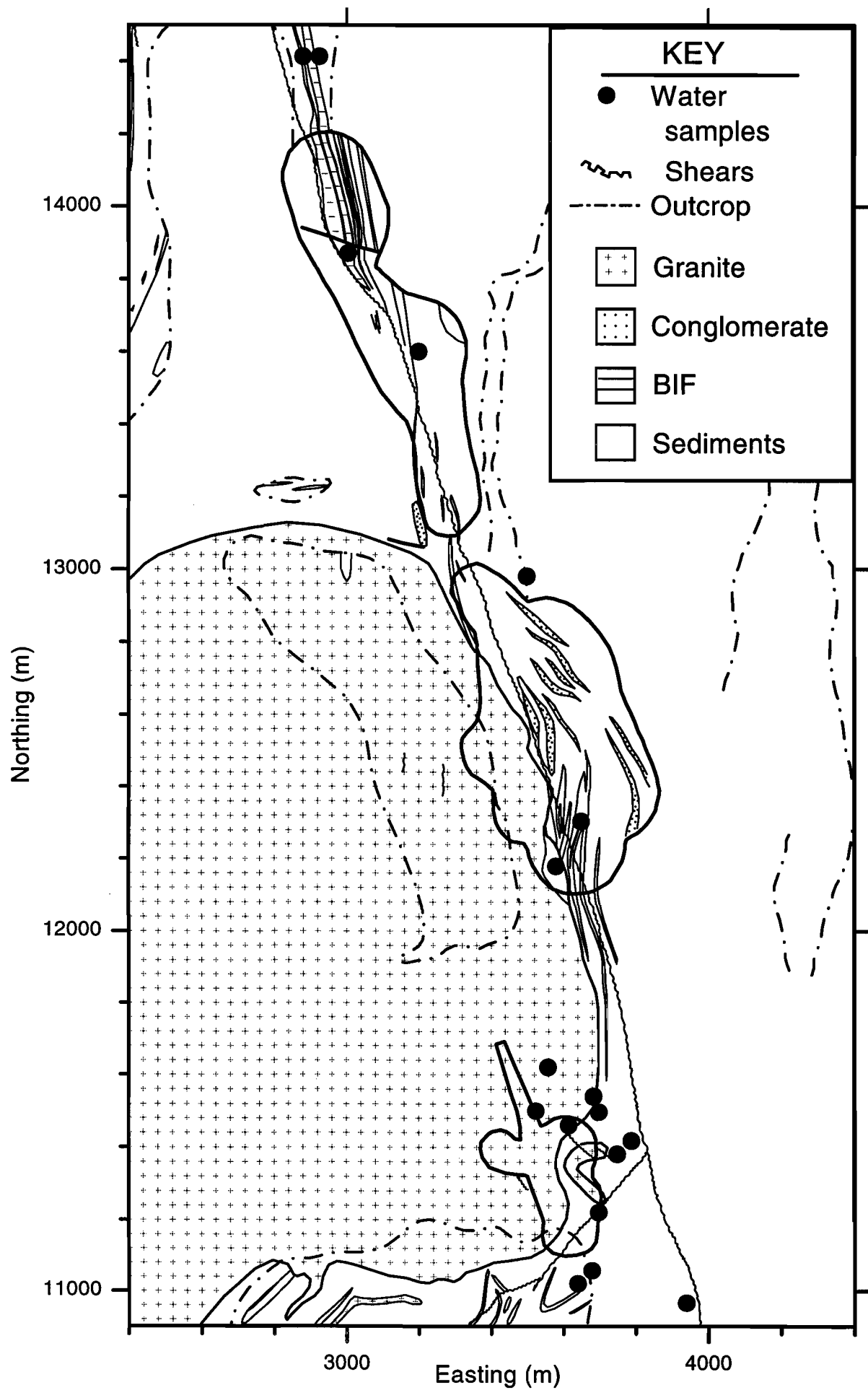


Figure 2: Local geology and water sampling sites at Granny Smith.

an assumption should be tested, as pH or Eh changes in water samples during transport could fundamentally change the trace element solubilities;

- (ii) a second sample that has been treated in the field (filtering and acidification) so as to ensure that final analyses will accurately reflect the original trace element composition of the groundwater. This slows down sampling, but is generally considered to enhance the accuracy and integrity of the data.

Table 1: Sample details for Granny Smith water samples.

Sample No.	Hole name	Easting (m)	Northing (m)	RL (m)	Method	Water Table (m)	Sampling Depth (m)
GS1	GSR904	3940	10965	nd	Bailed	17	25
GS2	GRC814	3640	11020	nd	Bailed	37 (60°)	55 (60°)
GS3	WEG 1	3679	11057	419.1	Bailed	nd	nd
GS4	WEG 2	3699	11220	418.7	Bailed	47	65
GS5	WEG 9	3749	11380	418.1	Bailed	45	65
GS6	WEG 7	3789	11416	419.7	Bailed	45	60
GS7	WEG 3	3616	11460	418.5	Bailed	40	55
GS8	Goanna Sth	3200	13600	345.0	Pumped	nd	nd
GS9	DW 15	3006	13870	365.5	Pumped	nd	nd
GS10	DW 7	3651	12304	345.2	Pumped	nd	nd
GS11	DW 22	3581	12178	360.0	Pumped	nd	nd
GS12	DW 16	3500	12980	422.8	Pumped	nd	nd
GS13	WEG 6	3525	11500	419.2	Bailed	39	55
GS14	WEG 8	3700	11496	418.5	Bailed	39	55
GS15	WEG 5	3685	11540	419.7	Bailed	42	55
GS16	WEG 4	3559	11620	418.6	Bailed	50	65
GS17	GRC800	2880	14413	~ 442	Bailed	68	80
GS18	GRC801	2925	14413	~ 442	Bailed	73	86

nd not determined

The filtered and acidified waters were analysed for Cu, Pb and Cd by anodic stripping voltammetry (ASV) at CSIRO Floreat Park Laboratories, for Na, Mg, Ca, K, SO₄, 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, I, Co, Ni, Cu, Zn, Ga, As, Y, Mo, Ag, Cd, Sn, Sb, rare earth elements (REE), W, Tl, Pb, Bi, Th and U by inductively coupled plasma - mass spectroscopy (ICP-MS) at the Mineral Science Laboratory, Chemistry Centre, WA.

The filtered and unacidified water samples were analysed for Cl by the Technicon Industrial method (Zall *et al.*, 1956) and for Br by high pressure liquid chromatography (HPLC; Paul Haddad, personal communication) at CSIRO Floreat Park Laboratories.

In addition, a 1 L sub-sample of the filtered water and a separate 1 L sub-sample of unfiltered water, were both acidified with 1 mL 15 M HNO₃ with addition of a 1 gram sachet of activated carbon. The bottles were rolled for eight days in the laboratory and the water then discarded. The carbon was then analysed for Au by neutron activation analysis (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 standards of varying concentrations, and in varying salinities, with activated carbon.

There were several unforeseen problems in the sampling:

- (i) Most of the exploration holes at Windich were unsuitable for sampling, as they were angled, with casing only part of the way down the hole, making loss of the sampler down the hole possible. Additionally, most of these angle holes were open, and therefore could have rainwater contamination, and had partially collapsed. Therefore, the holes finally sampled at Windich were the WEG holes prepared by Dames and Moore (which were deep, mostly capped, stabilized and vertical) and any other "good" drill holes. Unfortunately, these holes all tended to lie on the eastern edge of the proposed Windich pit.
- (ii) The Windich area was partly dewatered, which will disturb the hydrology of the site.
- (iii) It was not possible to find accessible drill holes in background Au areas, so as to provide a blank.

2.3 Speciation analysis

Speciation analysis involves computing parameters such as the solution species and degree of mineral saturation from the solution data, based on thermodynamic data. 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 Granny Smith samples, ion pairing effects become important and programs using the specific ion interaction model known as the Pitzer equations need to be used. The programs used were PHRQPITZ (courtesy USGS) which gives data for Na, K, Mg, Ca, Cl, HCO_3 and SO_4 , and PC-PHREEQEP (Crowe and Longstaffe, 1987) which was used to obtain further corrected parameters for Sr, Ba, Fe, Al and Mn. A sample output from PHREEQE is given in Appendix 5.

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

The determinations are important in understanding solution processes at the site. They have particular value in determining whether the spatial distribution of an element is correlated with geological and/or mineralization phenomena or whether they are related to weathering or environmental effects. Thus, if Ca distribution is controlled by equilibrium with gypsum in all samples, then the spatial distribution of dissolved Ca will reflect SO_4 concentration alone and have no direct exploration significance.

3 RESULTS

3.1 Comparison of analyses

Analytical results are compiled in Appendix 1. The total dissolved solids (TDS), a measure of groundwater salinity, were calculated from the major element contents. A number of the base metals were analysed using two or three techniques, with the comparison of the results given in Appendix 2. There was a very good agreement between methods for Co (Figure A2.1), Cu (ICP-AES and ASV, but not ICP-MS; Figures A2.3 and A2.4) and Zn (Figure A2.5). The agreement for Ni was poorer (Figure A2.2), presumably due to the poor sensitivity of ICP-AES for Ni, with Cd values being generally too low for good detection (Figure A2.6). Thus, the analytical results for Co, Ni, Cu and Zn are considered to have a high accuracy, with Ni ICP-AES and Cu ICP-MS results being rejected. Cadmium was below detection limit for most samples.

3.2 Comparison of the two sample treatments

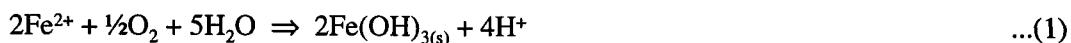
Two sample methods were used to investigate whether the simpler technique of filtering and acidifying in the laboratory [treatment (i), Section 2.2] gives adequate information compared with the more accepted method of filtering and acidifying water samples in the field immediately after sampling.

Comparative results for field filtered [treatment (i)] and laboratory filtered [treatment (ii)] techniques are shown in Appendix 3, Figures A3.1 - A3.30. A linear relationship indicates that both treatments gave similar results for that element. As the bailed samples generally had much higher suspended solids than the pumped samples and therefore may have significant solid:solution interactions during transport, the two different sampling techniques are shown as different symbols.

Agreement between the two sample treatment techniques is generally surprisingly good, although there is poorer linearity for those elements having very low concentrations [*i.e.*, Ti (Figure A3.9), Y (Figure A3.18), REEs (Figures A3.23 and A3.24), W (Figure A3.25), Tl (Figure A3.27) and Bi (Figure A3.29)], possibly due to higher analytical errors. In addition, there is poor agreement for Al, Fe and Au, as discussed below.

There was significant Al precipitation from those waters highest in Al, when the sample was not filtered and acidified in the field (Figure A3.7). Dissolved Al concentrations are generally low in neutral waters, and at Granny Smith the concentrations were even lower if the groundwaters were not filtered and acidified immediately. This may reflect higher Al concentrations due to groundwater processes releasing Al above equilibrium for Al oxides. For the treatment (i) samples this Al presumably precipitated or adsorbed on oxide surfaces during transit.

There was also major precipitation of Fe from waters that were not filtered and acidified in the field (Figure A3.11). This is presumably because Fe is originally present in ground water as ferrous ion, which is precipitated when the groundwater is oxidized:



Gold showed good agreement between the two sample treatment methods for the pumped samples, but poor agreement for the bailed samples (Figure A3.26). As Au sorbs strongly onto Fe oxide and other surfaces (Gray *et al.*, 1990), this may reflect solution-solid interactions in these high suspended solid samples during transit.

Although the dissolved concentrations of most of the elements appear not to be affected by filtering in the laboratory rather than directly after sampling, the strong effects on Fe, Al and Au, all of which

are highly significant for analysing groundwater processes (see below), leads to the recommendation that water samples should be filtered and acidified.

In the following sections, results are discussed for the treatment (ii) (*i.e.*, filtered and acidified in the field) samples only.

3.3 Chemistry of Granny Smith groundwaters

3.3.1 Comparison with results from other Yilgarn waters.

Averaged elemental data for the Granny Smith groundwater samples are given in Table 2. Also listed in Table 2 are data for sea water (taken from Weast *et al.*, 1984) and the averaged data for four other sites previously investigated:

- (i) Yalanbee, a non-mineralized area which lies some 50 km east of the western edge of the Yilgarn Block;
- (ii) Boags, a gold deposit at Bottle Creek, located 210 km north north-west of Kalgoorlie (central Yilgarn; Gray, 1992);
- (iii) Mount Gibson, a gold deposit about 100 km north-east of Dalwallinu (central-west Yilgarn; Gray, 1991);
- (iv) 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 Granny Smith and at other sites are plotted *versus* TDS or *versus* pH in Appendix 4, Figures A4.1 - A4.36. The sea water data are used to derive the line of possible values if sea water were diluted with freshwater or concentrated by evaporation, hereafter denoted as the sea water line, and shown as the dotted line. Where the dotted line is not shown, this is because the sea water concentration is too low, relative to the concentration of the element in groundwaters, to be observed on the graph.

Concentrations of the major elements (*e.g.*, Na, Mg, Ca, K, Cl, SO₄ and Br) and the minor elements are similar to those at the other mineralized areas. Gold concentration is low, particularly at Windich, in comparison with other sites, where even shallow waters contained appreciable Au.

3.3.2 Acidity and oxidation potential

An Eh-pH plot of waters from Granny Smith and other sites is shown in Figure 3. The Granny Smith groundwaters are near neutrality and have a similar Eh range to neutral waters from other sites. Waters from other sites with lower Eh values are generally Fe rich (Gray, 1990, 1991, 1992), as is observed here (Figure 4). Soluble Fe is commonly derived from the first stage of the oxidation of pyrite and other sulphide minerals:

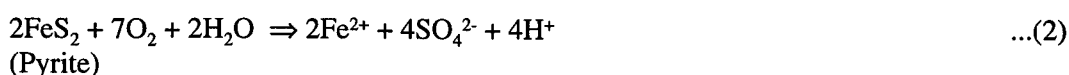


Table 2: Averaged elemental compositions of Granny Smith groundwaters, with results from other sites given for comparison.

Sample	Granny Smith (18) #		Yalanbee (3)		Boags (2)		Mt. Gibson (50)		Panglo (50)		Sea water
	Mean	Std Dev @	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	
pH	7.3	0.4	4.7	0.8	6.6	0.03	6.5	0.7	4.9	1.2	nd
Eh (mV)	250	82	300	50	160	30	310	100	490	180	nd
Na *	0.325	0.016	0.28	0.01	0.25	0.001	0.32	0.02	0.32	0.01	0.31
Mg *	0.024	0.005	0.057	0.002	0.052	0.002	0.033	0.007	0.032	0.003	0.040
Ca *	0.024	0.011	0.020	0.004	0.032	0.001	0.009	0.010	0.008	0.003	0.012
K *	0.0097	0.0027	0.0030	0.0002	0.0092	0.0001	0.0112	0.0018	0.0008	0.0003	0.0112
Cl *	0.46	0.06	0.60	0.01	0.47	0.004	0.53	0.03	0.59	0.01	0.56
SO ₄ *	0.13	0.04	0.045	0.001	0.172	0.002	0.075	0.016	0.053	0.005	0.065
Br *	0.0005	0.0004	0.0016	0.0001	0.0024	0.0000	0.0017	0.0002	0.0005	0.0001	0.0019
HCO ₃	188	36	nd	nd	620	50	260	240	50	60	142
TDS	13000	17000	8100	2800	21000	600	24000	46000	84000	27000	34000
Al	0.009	0.007	1.2	1.3	0.0	0.1	0.3	2.1	8	14	0.01
Si	17	10	28	3	7	1	30	11	8	12	3
Ti	0.001	0.001	nd	nd	nd	nd	nd	nd	nd	nd	0.001
Cr	<0.005	-	0.003	0.002	0.002	0.002	0.004	0.030	0.04	0.09	0.00005
Mn	0.4	0.4	1.2	0.7	0.035	0.021	1	4	3	4	0.002
Fe	0.4	0.8	0.7	0.3	0.07	0.10	3	10	0.5	1.4	0.01
Co	0.02	0.04	0.012	0.006	0.000	0.005	0.01	0.04	0.19	0.19	0.0003
Ni	0.05	0.07	0.01	0.01	0.00	0.01	0.01	0.05	0.26	0.27	0.005
Cu	0.02	0.05	nd	nd	0.007	0.009	0.01	0.03	0.08	0.06	0.003
Zn	0.07	0.10	nd	nd	0.015	0.014	0.06	0.20	0.3	0.8	0.01
Ga	0.001	0.001	nd	nd	nd	nd	nd	nd	nd	nd	0.00003
As	0.04	0.04	nd	nd	0.11	0.15	nd	nd	nd	nd	0.003
Sr	1.8	1.6	1.6	0.5	5.9	0.2	2.4	2.7	7	4	8
Mo	0.03	0.02	nd	nd	nd	nd	nd	nd	nd	nd	0.01
Y	0.0002	0.0003	nd	nd	nd	nd	nd	nd	nd	nd	0.0003
Ag	0.0002	0.0004	nd	nd	nd	nd	nd	nd	nd	nd	0.0003
Cd	0.001	0.003	nd	nd	0.009	0.006	0.004	0.014	0.000	0.005	0.0001
Sn	0.001	0.001	nd	nd	nd	nd	nd	nd	nd	nd	0.003
Sb	0.004	0.006	nd	nd	0.17	0.22	nd	nd	nd	nd	0.0003
I	0.9	0.5	0.05	0.06	2.1	0.7	0.5	0.9	0.5	0.4	0.06
Cs	0.003	0.003	nd	nd	nd	nd	nd	nd	nd	nd	0.0005
Ba	0.03	0.02	0.053	0.004	0.010	0.011	0.06	0.12	nd	nd	0.03
REE	0.002	0.006	nd	nd	nd	nd	nd	nd	nd	nd	nd
W	0.001	0.001	nd	nd	nd	nd	nd	nd	nd	nd	0.0001
Hg	0.0003	0.0005	nd	nd	nd	nd	nd	nd	nd	nd	0.00003
Tl	0.0002	0.0002	nd	nd	nd	nd	nd	nd	nd	nd	0.000005
Pb	0.007	0.017	nd	nd	0.005	0.007	0.13	0.28	nd	nd	0.00005
Bi	<0.0002	-	nd	nd	nd	nd	nd	nd	nd	nd	0.00002
Th	<0.0002	-	nd	nd	nd	nd	nd	nd	nd	nd	0.00005
U	0.009	0.025	nd	nd	nd	nd	nd	nd	nd	nd	0.003
Au	0.015	0.026	nd	nd	0.5	0.7	0.13	0.21	0.3	0.6	0.01

All concentrations in mg/L, except Au in µg/L.

Bracketed numbers denote the number of samples.

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

* For the elements Na, Mg, Ca, K, Cl⁻, SO₄²⁻ and Br⁻, the ratio of the element concentration to TDS is used rather than the concentration. (See Section 3.3.3 for details.)

nd not determined

- not applicable

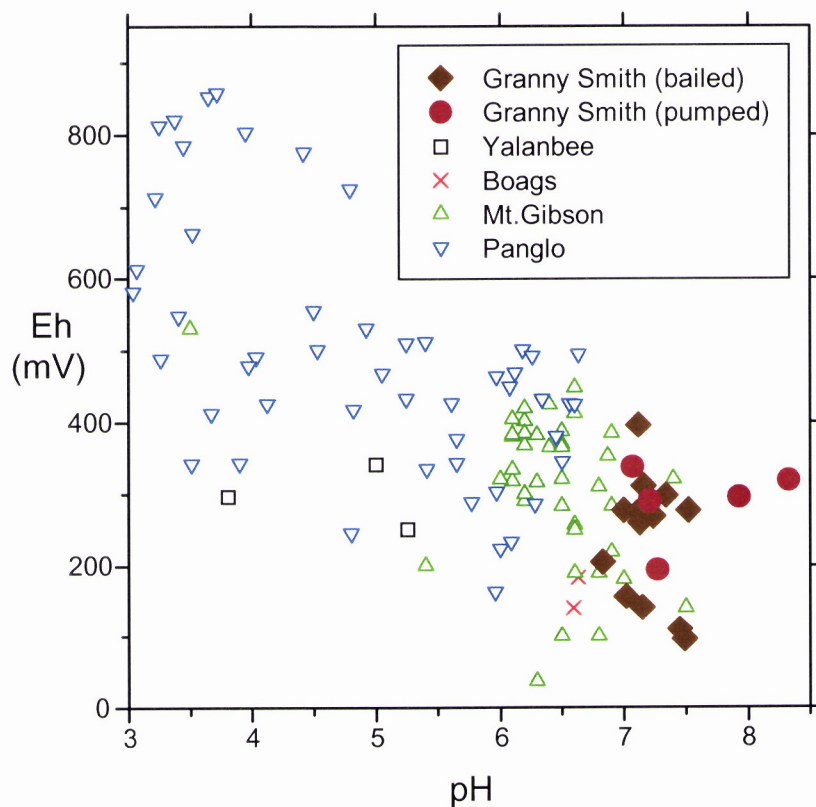


Figure 3: Eh vs. pH for groundwaters from Granny Smith and other sites.

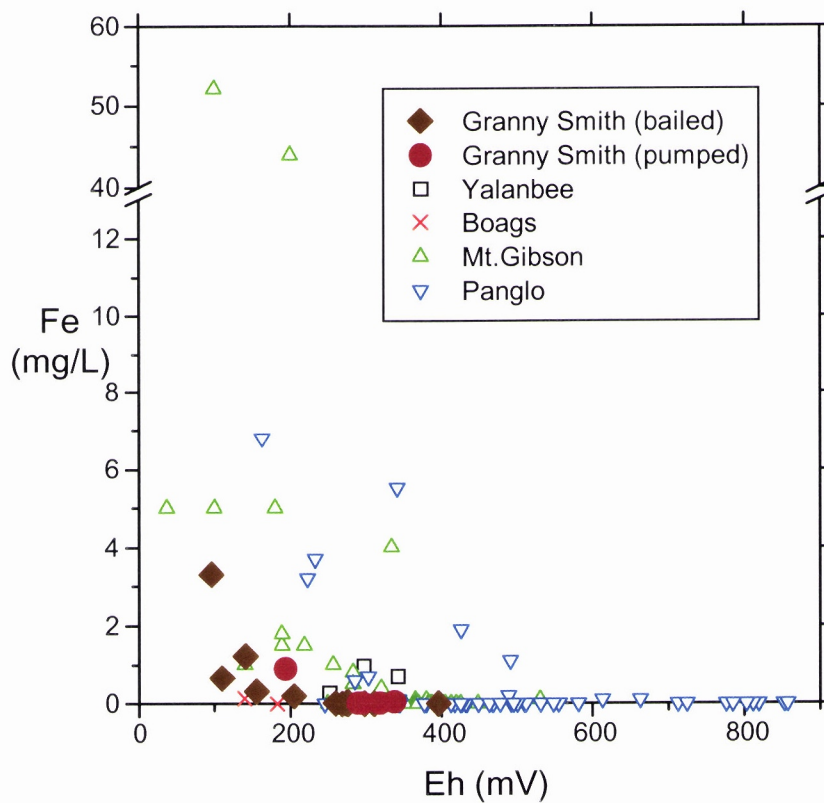


Figure 4: Dissolved Fe vs. Eh for groundwaters from Granny Smith and other sites.

At higher Eh values, Fe will tend to oxidize and precipitate (Eqn. 1), as appears to have occurred in the laboratory filtered samples (Section 3.2). The moderate concentrations of dissolved Fe and the neutral pH of the water samples indicate that sulphides may be oxidizing under neutral conditions. Under such a regime, significant concentrations of the intermediate sulphur compounds thiosulphate ($\text{S}_2\text{O}_3^{2-}$) and sulphite (SO_3^{2-}) are commonly produced (Granger and Warren, 1969; Goldhaber, 1983; Webster, 1984):



This may have consequences for the groundwater mobility of Au, as discussed in Section 3.3.5.

3.3.3 Major ion chemistry

For the ions Na, Mg, Ca, K, Cl, SO_4 and Br, the ratio of the concentration divided by TDS (hereafter called the TDS ratio) is used in Table 2 rather than the concentration. 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. The TDS ratios for most of the major elements diverge from that of sea water. Bromine (Figure A4.6) is highly depleted and Mg and K (Figures A4.2 and A4.5) are moderately depleted, relative to sea water. The relationships of these ions to TDS, though below the sea water line, are generally linear, suggesting them to be uniformly depleted throughout the entire study area. Depletions of these three ions were also observed at Panglo (Figures A4.2, A4.5 and A4.6) and were interpreted as being due to dissolution of previously deposited halite (NaCl ; Gray, 1990), which would increase the proportion of Na and Cl in the groundwater, and therefore reduce the proportion of other ions. Conversely, the Granny Smith groundwaters are enriched in SO_4 and Ca (Table 2), particularly in the less saline samples. This may be due to dissolution of gypsum:



and/or calcite:



which may lead to groundwater enrichment in Ca and SO_4 .

The potential for dissolution or precipitation of minerals such as gypsum from the Granny Smith 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 3, with SI values plotted in Appendix 5.2. As discussed in detail in Section 2.3, a SI of zero indicates the solution is saturated with respect to that mineral, a SI less than zero indicates under-saturation and a SI greater than zero indicates the solution is over-saturated with respect to the mineral phase.

The less saline Granny Smith groundwaters are undersaturated with respect to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; Figure A5.1), and may therefore dissolve any pre-existing gypsum, consistent with the observations of Ca and SO_4 enrichment in these samples (Eqn. 4). In addition, the groundwaters are undersaturated with respect to the Sr analogue [celestine (SrSO_4); Figure A5.2] and are commonly saturated with respect to barite (BaSO_4 ; Figure A5.3). All of the Granny Smith groundwaters are undersaturated with respect to halite (NaCl ; Figure A5.4). Similar controls on groundwater concentrations of these elements are observed for saline groundwaters at other sites (Gray, 1990, 1991, 1992). In comparison, the large negative and positive ranges in SI values for calcite and dolomite (Table 3, Figures A5.5 and A5.6) indicate little groundwater equilibration with these carbonate minerals.

Table 3: SI Values for the Granny Smith groundwaters, for a number of relevant solid phases.

Mineral	Formula	Lower	Upper	Mean	Standard Deviation
Halite	NaCl	-5.1	-1.9	-3.9	1.0
Gypsum	CaSO ₄ .2H ₂ O	-1.5	-0.3	-1.1	0.4
Celestine	SrSO ₄	-1.9	-0.9	-1.5	0.3
Barite	BaSO ₄	-0.9	0.3	-0.2	0.4
Calcite	CaCO ₃	-0.8	0.8	-0.3	0.4
Dolomite	CaMg(CO ₃) ₂	-1.1	2.4	0.0	0.9
Al(OH) ₃	Al(OH) ₃	-2.8	-1.1	-1.9	0.4
SiO ₂	SiO ₂	-1.0	-0.2	-0.6	0.3
Siderite	FeCO ₃	-5.4	0.5	-2.4	1.6
Ferrihydrite	Fe(OH) ₃	1.1	2.7	1.8	0.5
Rhodocrosite	MnCO ₃	-2.6	0.3	-0.9	0.9
CoCO ₃	CoCO ₃	-4.1	-2.0	-3.2	0.6
Ni(OH) ₂	Ni(OH) ₂	-4.6	-1.3	-3.4	0.9
Tenorite	Cu(OH) ₂ .H ₂ O	-1.2	0.2	-0.5	0.7
Smithsonite	ZnCO ₃	-3.2	-1.8	-2.6	0.5
Iodyrite	AgI	-2.6	-0.7	-1.8	0.7
Otavite	CdCO ₃	-2.1	-0.7	-1.4	0.5
Sb(OH) ₃	Sb(OH) ₃	-1.0	0.5	-0.5	0.5
Au Metal	Au	2.7	7.6	4.8	1.5
Cerrusite	PbCO ₃	-2.2	-0.7	-1.6	0.5
Schoepite	UO ₂ (OH) ₂ .H ₂ O	-6.3	-3.4	-5.1	0.7

The low Al concentration of the Granny Smith groundwaters is primarily due to the neutral pH conditions (Figure A4.13). Speciation analysis indicates that most groundwaters are slightly oversaturated with respect to gibbsite, but below saturation with respect to amorphous Al(OH)₃ (Figure A5.7). Dissolved Si concentrations are above that for sea water and approximately match other sites (Figure A4.14), with the groundwaters oversaturated with respect to quartz, and undersaturated with respect to amorphous silica (Figure A5.8). The bailed samples commonly have higher dissolved Si than the pumped samples, perhaps reflecting the presence of more soluble phases, such as opaline silica, closer to the surface.

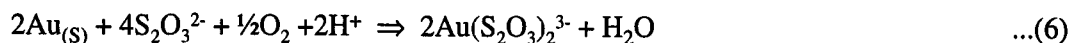
Dissolved Fe concentrations (Figure A4.16) match other sites. In a few cases, the groundwaters reach equilibrium with siderite (FeCO₃; Figure A5.9), a Fe^{II} carbonate, whereas in all cases the samples are moderately oversaturated with respect to ferrihydrite (Figure A5.10), a highly soluble Fe^{III} oxide mineral.

3.3.4 Minor element chemistry

Most of the minor elements (Table 2) have concentrations similar to those at other sites. The minor elements are generally undersaturated with respect to the least soluble mineral phase (Table 3; also see Figures A5.11 - A5.20), indicating little dissolution of these elements and/or removal from solution via mechanisms such as sorption. Exceptions are Cu (Figure A5.14), which is saturated with respect to tenorite [Cu(OH)₂.H₂O] in some samples, and Sb, which commonly reaches equilibrium with respect to Sb(OH)₃ (Figure A5.18).

3.3.5 Gold chemistry

Dissolved Au concentrations at Granny Smith are low, relative to other mineralized sites (Figure A4.30). On the basis of previous work (Gray, 1988 and references given therein), the most likely form of dissolved Au at Granny Smith is as the thiosulphate complex $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$. This is because the thiosulphate ion is commonly released during weathering of sulphide minerals under neutral conditions, which appear to match conditions at Granny Smith (Section 3.3.2). Once formed, thiosulphate will readily dissolve Au (Lakin *et al.*, 1974; Mann and Webster, 1990):



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 at Granny Smith are close to that of sea water.

The low Au concentrations may reflect retardation of Au dissolution, which may be due to the form of the mineralization, *i.e.*, if Au is protected by quartz veins then circulating groundwaters may not be able to access it. This phenomenon may also be due to the Granny Smith site representing a very mature weathering regime, with very low activity at the oxidation front. However, whatever the reason for the low dissolved Au at this site, the exploration potential of dissolved Au ALONE is not as great at Granny Smith as at some other sites. The hydrogeochemistry of Au will be discussed further in Section 4.4.

4 MAPPING OF THE DATA

4.1 Description of the mapping

Element distribution maps are shown in Appendix 6 and are discussed below. Note that outlines of the geology, pits and (as the dashed line) outcrop are included in each plot to facilitate interpretation. The geology is shown in more detail in Figure 2.

4.2 Salinity, pH and Eh

Total dissolved solids (Figure A6.1): The salinities of the samples vary widely, from 0.2 to 7% TDS. The increase in salinity moving south from the top of Goanna pit to the southern end of Granny Smith pit (based mainly on pumped samples) matches previous results from waters sampled during drilling. However, at Windich, the salinities of the bailed samples collected during this study (0.2 - 2.6% TDS) are markedly lower than those collected during drilling (20% TDS). The TDS distribution at Windich is also highly irregular, with order of magnitude changes over small areas. This suggests a stratified system in which fresher waters overlie more saline waters, with the salinity of the samples being dependant on the aquifer(s) being accessed. Thus, the more saline samples possibly represent the deeper groundwater, and the less saline samples represent the shallow groundwater system.

Acidity (Figure A6.2): The pH distribution is narrow (6.8 - 8.3), with the shallow Windich waters appearing to be slightly more acid than the deeper, more saline samples. The most alkaline samples are at the centre of Goanna pit and between Goanna and Granny pits.

Oxidation potential (Figure A6.3): The highest Eh values are observed in the two samples north of Goanna, possibly reflecting a control from the outcropping BIF in this area. Oxidation potentials appear to decline from the north to the south of the Windich area. This may be due to release of reducing compounds, such as Fe^{2+} , during weathering. However, such an interpretation is complicated by the recent dewatering that has disturbed the original groundwater flow patterns.

4.3 Major elements and ions

Bicarbonate (Figure A6.4): The range in HCO_3 concentrations is very narrow, relative to other sites (Figure A4.9). Possibly as a consequence of this, there are no observable patterns in HCO_3 distribution, except that the highest pH samples (Figure A6.2) were, as expected, highest in HCO_3 .

Magnesium, potassium and bromine (Figures A6.5 - A6.7): The Mg, K and Br data are shown in Figures A6.5 - A6.7 as the ratio over TDS (see Section 3.3.3). These ions are depleted in the Granny Smith waters (Figures A4.2, A4.5 and A4.6), particularly for the more saline samples. The Mg/TDS, K/TDS and Br/TDS ratios are highest (similar to the sea water ratios) for the least saline water samples (compare with Figure A6.1), and, in particular, for the two groundwater samples north of Goanna.

Sulphate (Figure A6.8): As discussed in Section 3.3.3, the groundwater enrichment in SO_4 may represent a contribution from the dissolution of gypsum. When expressed as a ratio, the enhancement, relative to sea water, is greatest in the least saline samples, due to a lower background SO_4 concentration, and a greater tendency for gypsum dissolution. Therefore, the variation in TDS (Figure A6.1) confuses any possible SO_4 /TDS pattern.

Calcium, strontium and barium (Figure A6.9 - A6.12): Like SO_4 , Ca is enriched in the Granny Smith groundwaters. The enrichment is strongest in the Windich area, possibly reflecting gypsum dissolution in the comparatively fresher waters (Eqn. 4). Such an enrichment is not immediately obvious for Sr when the elemental concentration is plotted (Figure A6.10), presumably due to

background salinity effects, because Sr is moderately abundant in normal saline waters. Calcium and Sr would be normally expected to have proportionally similar concentrations (Figure 5): however, a plot of the Sr/Ca ratio (Figure A6.11) indicates that Sr is enriched at Windich. Barium is also enriched in Windich samples (Figure A6.12), though this may merely be a reflection of the control of dissolved Ba via barite (Section 3.3.3; Figure A5.4).

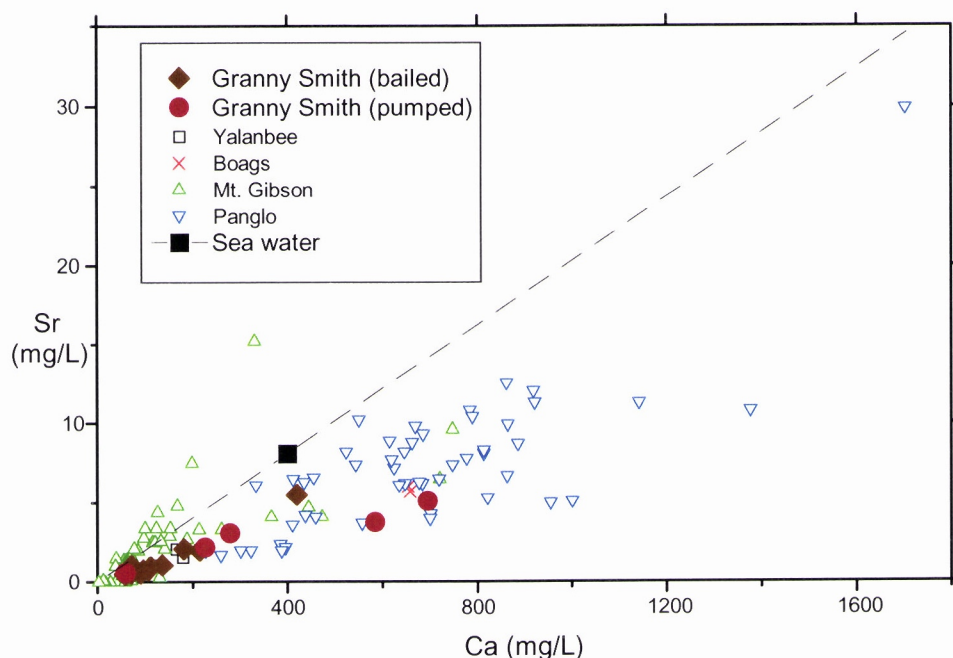


Figure 5: Strontium vs. Ca for groundwaters from Granny Smith and other sites.

Iron (Figure A6.13): Iron is also enriched in Windich groundwaters, possibly due to release during oxidation of pyrite and/or other sulphide minerals (Eqn. 2).

Silicon, aluminium and gallium (Figures A6.14 - A6.16): The enrichment of Si and Al in Windich groundwaters may be due to release of these elements from feldspars or kaolinite during acid conditions produced during sulphide oxidation. The decreases in dissolved Al concentration observed for the samples that were not filtered in the field (Section 3.2; Figure A3.7) suggest this high Al content to be greater than expected for normal groundwater conditions. Gallium is also enriched in Windich groundwaters (Figure A6.16), possibly because its geochemistry is similar to Al.

4.4 Minor elements

Gold (Figures A6.17 and A6.18): As discussed previously (Section 3.3.5), dissolved Au concentrations are low, relative to other site investigations. The Au distribution map (Figure A6.17) indicates the highest Au concentrations occur in the pumped samples from the southern part of Granny, with the sample from the central part of Goanna also having moderate Au concentrations. When compared to the Au grade in the solid (Figure A6.18), there is a broad correlation between Au grade and dissolved Au for the samples from Goanna and Granny. However, at Windich the dissolved Au concentrations are uniformly low, even in areas of high Au grade. This may be because the Windich samples are from the shallow groundwater system (Section 4.2), whereas the Au mineralization occurs at depth (Section 2.1). Thus, the groundwaters being sampled at Windich are not in direct contact with the mineralization. Assuming strong stratification of the groundwater system, as appears to be the case, then little mixing of groundwaters will occur and samples of the shallow groundwater would be expected to have low Au concentrations.

Elements associated with Au (As, Sb, Tl) (Figures A6.19 - A6.21): These elements are commonly associated with primary Au, and their distributions do approximately match that of Au: in particular in that they are enriched in the southern part of Granny. In addition, the data appears to indicate that much of the mineralized area is enriched in As (Figure A6.19), suggesting that this element might have value as a regional groundwater pathfinder, though clearly further sampling distant from the mineralization would be required to demonstrate this.

First row transition/base metals (Mn, Co, Ni, Cu, Zn, Pb) (Figures A6.22 - A6.27): Most of these elements are particularly enriched in the two samples at the southern end of Granny pit, matching the Au distribution, with the exception of Cu (Figure A6.25), which is not enriched at Granny, but instead shows an enrichment in three of the Windich waters, and Zn (Figure A6.26) which is enriched both in Granny and Windich samples. The correlation of many of these elements with the Au distribution may reflect the occurrence of Ni, Pb and Zn in sulphide minerals, and Co and Mn in carbonates, which may be dissolved as a result of acidity originating from sulphide oxidation.

Molybdenum and tungsten (Figures A6.28 - A6.29): These two elements lie below Cr in the periodic table and have similar co-ordination chemistry. However, they differ in that Mo in nature is mostly found as a sulphide (*e.g.*, MoS₂), whereas W is usually found as oxygen compounds (Goldschmidt, 1954). This may explain the different groundwater distributions of these elements at Granny Smith: Mo (Figure A6.28) has a similar distribution to Au, associated elements (As, Sb, Tl) and elements commonly found in sulphides (*e.g.*, Ni, Pb and Zn); whereas W is most enriched in the Windich area (Figure A6.29).

Rare earth and associated elements (REE, Y, U) (Figures A6.30 - A6.32): The individual REE have similar distributions; for simplicity, the distribution of the total REE only is shown in Figure A6.30. The individual REE, Y and U are all significantly anomalous in a single sample at about 3600mE, 11000mN. This REE/Y/U anomaly is only observed in this one sample, for which only a field filtered sub-sample was available. Thus, the result is questionable, though if real presumably represents an intersection with REE and U enriched rocks.

Other elements (I, Cs, Bi, Hg, Sn) (Figures A6.33 - A6.37): There are no clear distribution patterns for these elements. Dissolved I and Cs (Figures A6.33 - A6.34) are highly enriched, relative to sea water (Figures A4.10 and A4.11), throughout the study area and, like As, may have scope as regional pathfinders. Concentrations of Bi, Hg and Sn (Figures A6.35 - A6.37) are low and therefore the precision may be very poor. This is also suggested by the poor agreement between laboratory and field filtered measurements (Figures A3.21 and A3.29).

4.5 General distribution patterns

The TDS data suggest that the groundwater system is stratified, with a saline system at depth and fresher waters (with possible mixing from rain water) closer to the surface (Section 4.2). The pumped samples at Goanna and Granny are from this deeper system, whereas the bailed samples taken at Windich are generally sampling the shallow groundwater system. As mineralization at Windich generally occurs at depth, then the groundwaters being sampled may not be those contacting Au-rich lithologies. This may explain why the concentration of dissolved Au and other aqueous pathfinder elements is very low for the sampled Windich groundwaters. The groundwaters at Windich are relatively enriched in Fe, Zn and Cu, possibly released during weathering of sulphide minerals, Si, Al and Ga, possibly released during transient acid conditions, Ca, Sr and Ba, possibly from dissolution of carbonates and W (though at a generally low concentration).

Mineralization at Goanna and Granny does occur into the weathered zone, and significant concentrations of dissolved Au are observed where the Au grades are high. Other elements that

appear to be associated with Au in the groundwater are As, Co, Mn, Mo, Ni, Pb, Sb, Tl and Zn. Arsenic, Mo, Sb and Tl are commonly associated with Au, and dissolved As and Sb appear to be useful pathfinders for Au mineralization at Boags (Gray, 1992); Pb and Zn enrichments may reflect galena and sphalerite associated with primary mineralization; and Mn, Co and Ni are enriched in groundwater associated with mineralization at the Hornets pit, Mt. Gibson gold deposit (Gray, 1991). Thus this multi-element association is not unique and may offer scope for mine-scale exploration.

Dissolved As, I and Cs are generally dispersed in the sample area. Other work has suggested that As and I are more broadly dispersed in groundwater than Au or Sb. Further sampling distant from mineralization would be required to test whether dissolved As, I or Cs have value as regional pathfinders.

5 DISCUSSION

On the basis of the results presented here, it would appear that there are significant problems for the use of hydrogeochemistry for Au exploration in this area. The dissolved Au concentrations at this site are generally low, relative to other sites (Figure A4.30). The reason for the difference is unclear, and thus difficult to compensate for in comparing between sites. Therefore, in a regional groundwater survey analysing for Au only, this area might well be discounted. There may, however, be some scope for a multi-element approach. Several elements (As, Co, Mn, Mo, Ni, Pb, Tl and Zn) appear to have potential as soluble pathfinders for Au, and their association with Au has been observed in groundwaters at other sites.

The very poor hydrogeochemical response to the mineralization at Windich, in comparison to the reasonably anomalous groundwaters found at Goanna and Granny, is of particular concern. As discussed in Section 4.5, this is possibly a consequence of the shallower groundwater sampling and the deeper position of the mineralization at Windich. The apparent major sensitivity of the groundwater signature tends to suggest that hydrogeochemistry would not work successfully as an exploration method in such environments.

The groundwater investigations at Granny Smith have been of interest, as they are being conducted in an area north of the Menzies line, in contrast with previous groundwater studies done further south. The project yielded "negative" results, which are only partially understood. Further work in similar, though hopefully less disturbed areas, may be of value in fully understanding the hydrogeochemistry of deposits in this region.

6 SUMMARY AND CONCLUSIONS

The hydrogeochemistry of the Granny Smith deposit was investigated, using two different sample treatments:

- (i) collecting waters and filtering and acidifying in the laboratory about 10 days later;
- (ii) filtering and acidifying in the field.

Agreement between the two methods was generally good, with the exception of Al, Fe and, to a lesser extent, Au (Section 3.2). This suggests that Al and Fe are precipitated during storage of the treatment (i) samples by oxidation/hydrolysis (Eqn. 1). Gold may be being lost during storage via sorption. The strong effects on Fe, Al and Au, all of which are highly significant for determining groundwater processes, leads to the recommendation that water samples should be filtered and acidified immediately after sampling whenever practicable.

Groundwaters are generally of neutral pH, with a similar Eh and dissolved Fe range to other sites (Section 3.3.2). The major ions Mg, K and Br are depleted in the Granny Smith groundwaters, relative to sea water (Section 3.3.3), suggesting dissolution of previously precipitated halite. The less saline waters are also enriched in Ca and SO₄, possibly due to a contribution from gypsum dissolution. The concentration of Ba appears to be controlled by equilibration with barite.

The concentrations of most of the minor elements are similar to other sites previously investigated (Section 3.3.4). By contrast, dissolved Au concentrations at Granny Smith are several orders of magnitude lower than those observed elsewhere, and indeed are not much higher than sea water (Section 3.3.5). The reasons for this are not clearly understood, but diminish the possibility of using dissolved Au at this site as an exploration medium.

The groundwater system appears to be highly stratified. The pumped samples at Goanna and at Granny are presumably sampling from deeper, more saline, aquifers, whereas the bailed samples at Windich appear to be generally sampling shallow, fresher water. At Windich, the Au mineralization occurs at depth and the sampled waters do not appear to be in contact with the mineralization, leading to a barren signature in the samples (Section 4.5). At Goanna and Granny, the deeper samples appear to be contacting Au mineralization, and the waters are enriched in Au (relatively to Windich), As, Co, Mn, Mo, Ni, Pb, Sb, Tl and Zn (Section 4.4). These enrichments can be related to understood processes, and are comparable with results from other sites (Section 4.5).

The exploration potential of groundwater appears to be poor at this site, particularly if only dissolved Au is considered. However, there may be some scope for a multi-element approach involving elements (As, Co, Mn, Mo, Ni, Pb, Tl and Zn) with potential as pathfinders for Au. In addition, As, I or Cs may have value as regional pathfinders.

ACKNOWLEDGMENTS

I would like to thank many of the staff of Placer Exploration. Mr Greg Hall was involved in the initiation and formulation of the project, while Peter Silversmith and Steve Hunt gave much assistance throughout the project.

CSIRO staff who assisted in the analysis of waters included G.D. Longman, J.K. Hosking and T.T. Pham at Floreat Park and L. Dotter at North Ryde. Additional analyses were performed courtesy of R.J. Watling and D. Delev of the Mineral Science Laboratory, Chemistry Centre WA, and carbons were analysed by Becquerel Laboratories at Lucas Heights. Finally, C.R.M. Butt gave extensive advice in the preparation of this report.

REFERENCES

- Bergeron, M. and Choinère, J., 1989. L'or dans les eaux souterraines: implications pour l'exploration. *J. Geochem. Explor.*, 31: 319-328.
- Cidu, R. and Edmunds, W.M., 1990. Preliminary studies of a hydrogeochemical method for gold prospecting - results from the United Kingdom. *Trans. Instn Min. Metall. (Sect. B: Appl. earth sci.)*, 99: Sept-Dec 1990.
- Crowe, A.S. and F.J. Longstaffe, 1987, Extension of geochemical modelling techniques to brines: coupling of the Pitzer equations to PHREEQE, in: *Proceedings of Solving Ground Water Problems with Models*, NWWA Conference, Feb. 10-12, 1987, Denver, Colorado, pp 110-129.
- Dekkers, M.J., Vriend, S.P., van der Weijden, C.H. and van Gaans, P.F.M., 1989. Uranium anomaly evaluation in groundwaters: a hydrochemical study in the Nisa region, Portugal. *Applied Geochemistry*, 4: 375-394.
- Dissanayake, C.B. and Weerasooriya, S.V.R., 1986. Fluorine as an indicator of mineralization - hydrogeochemistry of a Precambrian mineralized belt in Sri Lanka. *Chemical Geology*, 56: 257-270.
- Drever, J.I. (1982). "The Geochemistry of Natural Waters." (Prentice-Hall, Inc., Englewood Cliffs, N.J. U.S.A.). 388 p.
- Giblin, A.M. and Snelling, A.A., 1984. Application of hydrogeochemistry to uranium exploration in the Pine Creek Geosyncline, Northern Territory, Australia. *J. Geochem. Explor.*, 19: 33-55.
- Goldhaber, M.B., 1983. Experimental study of metastable sulfur oxyanion formation during pyrite oxidation at pH 6-9 and 30°C. *Amer. J. Sci.*, 283: 193-217.
- Goldschmidt, V.M., 1954. "Geochemistry." (Oxford Press, London). 730 p.
- Granger, H.C. and Warren, C.G., 1969. Unstable sulfur compounds and the origin of roll-type uranium deposits. *Econ. Geol.*, 64: 160-171.
- Gray, D.J., 1988. The Aqueous Chemistry of Gold in the Weathering Environment. (AMIRA P240/P241). CSIRO Division of Exploration Geoscience Restricted Report EG 4R. 64 p.
- Gray, D.J., 1990. Hydrogeochemistry of the Panglo Gold Deposit. (AMIRA P241: Weathering Processes). CSIRO Division of Exploration Geoscience Restricted Report 125R. 74 p.
- Gray, D.J., 1991. Hydrogeochemistry in the Mount Gibson Gold District. (AMIRA P240: Laterite Geochemistry). CSIRO Division of Exploration Geoscience Restricted Report 120R. 80 p.
- Gray, D.J., 1992. Hydrogeochemistry of Sulphide Weathering at Boags Pit, Bottle Creek, Western Australia. (AMIRA P241A: Weathering Processes). CSIRO Division of Exploration Geoscience Restricted Report 237R. 13 p.
- Gray, D.J., Lintern, M.J. and Longman, G.D., 1990. Chemistry of Gold in some Western Australian Soils. (AMIRA P241: Weathering Processes). CSIRO Division of Exploration Geoscience Restricted Report 126R. 62 p.
- Hall, G.C. and Holyland, P.W., 1990. "Granny Smith gold deposit." In *Geology of the Mineral Deposits of Australia and Papua New Guinea* (Ed. F.E. Hughes), pp. 519-524 (The Australasian Institute of Mining and Metallurgy: Melbourne).
- Hall, G.E.M., Vaive, J.E. and Ballantyne, S.B., 1986. Field and laboratory procedures for determining gold in natural waters: relative merits of preconcentration with activated charcoal. *J. Geochem. Explor.*, 26: 191-202.
- Hamilton, T.W., Ellis, J., Florence, T.M. and Fardy, J.J. (1983). Analysis of gold in surface waters from Australian goldfields: An investigation into direct hydrogeochemical prospecting for gold. *Econ. Geol.*, 78: 1335-1341.
- Lakin, H.W., Curtin, G.C. and Hubert, A.E., 1974. Geochemistry of gold in the weathering cycle. *U.S. Geol. Surv. Bull.* 1330, 80 p.
- Lintern, M.J. and Butt, C.R.M., 1993. The distribution of gold and other elements in soils at the Granny Smith gold deposit, Western Australia. (AMIRA P241A: Weathering Processes). CSIRO Division of Exploration Geoscience Restricted Report 385R. 73pp.
- McHugh, J.B., 1988. Concentration of gold in natural waters. *J. Geochem. Explor.*, 30: 85-94.

- Mann, A.W. and Webster, J.G., 1990. Gold in the Exogenic Environment. In "Geology of the Mineral Deposits of Australia and Papua New Guinea." (Ed. F.E. Hughes) pp 119-126. (The Australasian Institute of Mining and Metallurgy: Melbourne).
- Morris, B.J., 1982. Groundwater hydrogeochemistry in South Australia and its application to mineral exploration. Quarterly Geological Notes, Geological Survey of South Australia v82: 7-12.
- Parkhurst, D.L., Thorstenson, D.C. and Plummer, L.N. (1980). PHREEQE, a computer program for geochemical calculations. U.S. Geol. Surv. Water Resources Investigations 80-96, 210p.
- Runnels, D.D., 1984. Workshop 3: Hydrochemistry in mineral exploration. J. Geochem. Explor., 21: 1-3.
- Weast, R.C. (1983). CRC Handbook of Chemistry and Physics, 63rd Edition. CRC Press, Inc., Boca Raton, Florida.
- Webster, J.G., 1984). Thiosulphate complexing of gold and silver during the oxidation of a sulphide-bearing carbonate lode system, Upper Ridges Mine, P.N.G. A.I.M.M. Perth and Kalgoorlie Branches, Regional Conf. on "Gold Mining, Metallurgy and Geology", Oct 1984.
- Zall, D.M., Fisher, D. and Garner, M.D., 1956. Photometric determination of chlorides in water. Analytical Chemistry, 28:1665.