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HYDROGEOCHEMISTRY OF SULPHIDE WEATHERING AT BOAGS PIT, BOTTLE CREEK, WESTERN AUSTRALIA

D.J. Gray

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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.

PREFACE

The continuation of AMIRA Project 241 (Gold and associated elements in the regolith - dispersion processes and implications for exploration) has as an objective further investigations of the hydrogeochemistry of gold and the determination of characteristics useful for exploration for supergene and primary gold deposits.

The hydrogeochemical observations of the Boags gold Pit at Bottle Creek described in this report represent a relatively minor investigation. However, they are of value because they provide data that contribute to our understanding of the hydrogeochemical conditions of sulphide weathering. Specifically, the study:

(i) demonstrates the existence of environments that permit the dissolution of gold and other trace elements during sulphide weathering;

(ii) describes the characteristics of one such groundwater environment;

(iii) discusses how the waters may evolve as they move away from the specific environment

This study is complementary to investigations of the regolith geochemistry at the site, and the nature and surface expression of gold mineralization. Together they address many of the principal objectives of the Project.

C.R.M. Butt,
Project Leader.
March, 1992

ABSTRACT

Hydrogeochemical sampling of the Boags Open Pit at Bottle Creek was conducted by collecting groundwaters thought to be in contact with zones where sulphide minerals were weathering in non-acid conditions. The near neutral pH and the chemical characteristics of the two water samples were consistent with this assumption. The elements that are anomalously high in these samples, and their possible source are:

(i)   Ca, Mg and HCO_3^-, derived from dissolution of carbonate minerals;

(ii) SO_4^{2-}, As, Cd and Sb, released during oxidation of sulphide, arsenide and antimonide minerals;

(iii) I^- and (possibly) Br^-, which have been observed to be extensively enriched in sulphide environments;

(iv) Au, dissolved as the $S_2O_3^{2-}$ complex, as $S_2O_3^{2-}$ is released during neutral oxidation of sulphide.

Various mechanisms are postulated to dissipate these anomalies as groundwater disperses from the weathering sulphide body:

(i)   Ca, Mg, HCO_3^-, SO_4^{2-} and Br^- are already present in the saline groundwater and the anomalies will be dissipated via dilution, acidification, and precipitation of calcite, gypsum or Al sulphates. Thus, any enrichment of these ions in groundwaters in the surrounding strata tend to be subtle and not easily distinguished;

(ii) As, Cd and Sb can be lost from solution via a variety of reactions such as precipitation or adsorption;

(iii) I^- is highly soluble, with the major loss from solution being via oxidation to I_2 (Fuge, 1990). This reaction is expected to be slow and, given the low background of I^-, the I^- anomaly is expected to only be slowly diluted out and is commonly observed in mineralized areas (Gray, 1990, 1991);

(iv) The extent of the Au anomaly is highly dependant on solution conditions. If conditions remain neutral or only weakly acidic then the $Au(S_2O_3)_2^{3-}$ complex may have a moderate mobility. However, if the waters are Fe-rich then oxidation in the upper part of the regolith can lead to waters with pH values down to 3. Under such conditions $Au(S_2O_3)_2^{3-}$ will be destabilized and Au precipitated. If conditions are sufficiently oxidizing, then Au may dissolve as the chloride complex. However, this is a secondary reaction, which is not direct related to the initial sulphide weathering reactions as observed at Boags.

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LIST OF ABBREVIATIONS

L   litre
mL   milli-litre
$\underline{M}$ moles/litre
Eh   Oxidation Potential
SI   Solubility Index = Log [(Ion Activity Product)/(Activity Product for Equilibrium)]
                    (Measure of Over- or Under-saturation)
TDS   Total Dissolved Solids (Salinity)

LIST OF COMPOUNDS

Bicarbonate HCO_3^-
Gold chloride $AuCl_2^-$
Sulphate SO_4^{2-}
Thiosulphate $S_2O_3^{2-}$

LIST OF MINERALS

Calcite $CaCO_3$
Gypsum $CaSO_4 \cdot 2H_2O$
Halite $NaCl$
Magnesite $MgCO_3$
Pyrite FeS_2
Quartz SiO_2

1. Introduction

This report describes the results of limited water sampling at the Boags Open Pit (Bottle Creek). Specific fields of interest are:

(i) use of gold and other pathfinder elements in water as an exploration tool;

(ii) what ions cause mobility of gold, and how these ions are influenced by groundwater chemistry and water-rock interactions;

(iii) further understanding of the chemical and geological factors influencing the chemistry of waters in the Yilgarn Block;

(iv) development of techniques for analysis of groundwater data from mineralized areas;

(v) interaction with laboratory investigations and other site studies.

This work was compared with other investigations of the hydrogeochemistry of other gold-rich areas in the Yilgarn Block (Gray, 1990, 1991). The results of this work contribute to a compilation of data for mineralized and unmineralized regions in the Yilgarn Block. This compilation will advance our knowledge of groundwater characteristics, particularly in reference to the formation of geochemical haloes in the regolith and the use of groundwaters in exploration.

2. Methodology

2.1. SITE CHARACTERISTICS

The Bottle Creek gold deposit is located 210 km north northwest of Kalgoorlie and 77 km northwest of Menzies at longitude 120° 27'E and latitude 29° 10'S. It occurs within the Archaean Coolgardie-Mt. Ida greenstone belt to the west of the Norseman-Wiluna greenstone belt.

Mineralization occurs within altered and metamorphosed easterly-dipping basaltic volcanics which have been intruded by quartz porphyry. Massive sulphides, hosted by a possible graphitic shale, have been weathered to a depth of approximately 85 m, to form a gossan that outcrops sporadically over a strike length of 26 km.

The deposit is situated within a broad valley flanked by a BIF ridge to the west and lateritic breakaways developed over granite to the east. Bottle Creek drains to the south. The essentially flat valley floor has a covering of alluvium and colluvium consisting of red soil and variably cemented pisolitic hardpan and calcrete, and a lag of surface pisoliths. The climate is semi-arid with an annual rainfall of about 300 mm.

Initial mineralogical and geochemical analyses of gossans and mineralized wall rocks from Emu, VB and Boags prospects are described in Taylor (1989).

2.2. WATER SAMPLING AND ANALYSIS

Sampling was done in late 1990. Two samples were taken: "Boags North" was sampled from an operating dewatering bore on the northern part of the pit; and "Boags South" was sampled from a bore hole on the southern part of the pit, using a specially designed pump sampler.

Waters were analysed for pH, temperature, conductivity, and oxidation potential (Eh) at the time of sampling. A 125 millilitre (mL) water sample was collected in a polythene bottle (with overfilling to remove all air) for later HCO_3^- analysis by alkalinity titration in the laboratory. About 2.5 litres (L) of water was filtered through a $0.45\mu m$ membrane filter in the field. About 100 mL of the filtered solution was acidified [0.1 mL 15 moles/litre ($\underline{M}$) nitric acid (HNO_3)], and analysed for Na, Mg, Ca and K by Atomic Absorption Spectrophotometry and for Cu, Zn, Pb and Cd by Anodic Stripping Voltammetry at CSIRO Floreat Park Laboratories, and for Co, Al, Fe, Mn, Ba, Cr, Ni, Sr and Si by Inductively Coupled Plasma - Atomic Emission Spectroscopy at CSIRO North Ryde Laboratories.

In addition, about 50 mL of the filtered water was collected separately, and analysed by Ion Chromatography at CSIRO Floreat Park Laboratories, for Cl^-, Br^- and SO_4^{2-}, using a DIONEX AS4A column under standard eluent conditions (Dionex, 1985) with a conductivity detector, and for I^- and thiosulphate using a DIONEX AS5 column under standard eluent conditions (*ibid.*) with an electrochemical detector. Thiosulphate concentration was below detection (0.1 mg/L) in both samples.

Two 1 L sub-samples of the filtered water were mixed with 1 mL 15 $\underline{M}$ HNO_3 and a 1 g sachet of activated carbon. The bottles were rolled for eight days in the laboratory and the water then discarded. The activated charcoal was then analysed for Sb, As, and Au by Neutron Activation Analysis at Bequerel Laboratories and for Sb, Ag, Bi, Hg and V by X-ray Fluorescence at CSIRO Floreat Park Laboratories. Laboratory investigations have indicated that 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.

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

3. Results and Discussion

Elemental data for the two samples are listed in Table 1. The total dissolved solids (TDS) given in the table was calculated from the major element contents. Also listed in this table are data for sea water (taken from Weast *et al.*, 1984) and the averaged data for three other sites previously investigated: Bakers Hill, which lies some 50 km east of the western edge of the Yilgarn Block; Mount Gibson, a gold deposit about 100 km northeast of Dalwallinu (central-west Yilgarn; Gray, 1991); and Panglo, a gold deposit some 30 km north of Kalgoorlie (south Yilgarn; Gray, 1990).

An Eh-pH plot of waters from Boags and other sites is shown in Figure 1. The Boags samples are near neutrality and have relatively low Eh values. The Mount Gibson and Panglo samples that plot in this zone are all waters that were sampled at depth and are generally Fe rich. Soluble Fe is probably derived from the first stage of the oxidation of pyrite and other sulphide minerals:

$$2FeS_2 + 7O_2 + 2H_2O \Rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad ...(1)$$
(Pyrite)
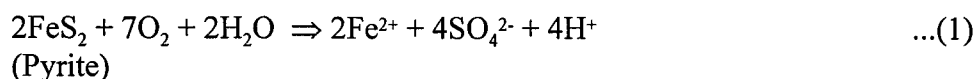
The acid production from this reaction is neutralized if there are carbonate minerals present, *e.g.*:

$$CaCO_{3(S)} + H^+ \Rightarrow Ca^{2+} + HCO_3^- \qquad ...(2)$$
(Calcite)

resulting in high Ca and HCO_3^- concentrations, as observed at Boags. The mineralized zone at Boags is carbonate-rich (Kitto, personal communication), consistent with such a sequence of events occurring here. Speciation analysis (Section 4) indicates that the waters are at equilibrium with calcite and magnesite ($MgCO_3$), further supporting this hypothesis.

Under these conditions, intermediate products of sulphur oxidation such as thiosulphate ($S_2O_3^{2-}$) and sulphite (SO_3^{2-}) are commonly formed:

$$FeS_2 + \frac{3}{2}O_2 \Rightarrow Fe^{2+} + S_2O_3^{2-} \qquad ...(3)$$

(Listova *et al.*, 1968; Granger and Warren, 1969; Goldhaber, 1983; Webster, 1984). These compounds have a high stability in neutral and alkaline conditions (Rolla and Chakrabarti, 1982) and have a particular importance in Au hydrogeochemistry due to the very high solubility of the Au thio complexes, as described below.

The second stage of pyrite oxidation, which occurs closer to the surface, is the oxidation and hydrolysis of Fe:

$$2Fe^{2+} + \frac{1}{2}O_2 + 5H_2O \Rightarrow 2Fe(OH)_{3(s)} + 4H^+ \qquad ...(4)$$
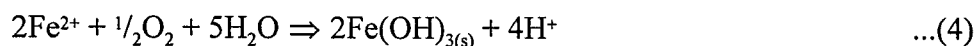
resulting in the acid groundwaters observed at the other sites (Fig. 1).

Table 1: Elemental Compositions of Boags Pit waters, with averaged analyses from other sites given for comparison.

Sample	Boags (2) [#]				Bakers Hill (3)		Mt. Gibson (50)		Panglo (50)		Sea water	
	North	South	Mean	Sd Dv[@]	Mean	Sd Dv	Mean	Sd Dv	Mean	Sd Dv	Conc.	Ratio
pH	6.59	6.63	6.61	0.03	4.68	0.78	6.5	0.7	4.9	1.2		
Eh (mV)	140	183	160	30	300	50	310	100	490	180		
Na *	5150	5320	0.25	0.001	0.28	0.01	0.32	0.02	0.32	0.01	10500	0.31
Mg *	1104	1086	0.052	0.002	0.057	0.002	0.033	0.007	0.032	0.003	1350	0.040
Ca *	654	658	0.032	0.001	0.020	0.004	0.009	0.010	0.008	0.003	400	0.012
K *	192	196	0.0092	0.0001	0.0030	0.0002	0.0112	0.0018	0.0008	0.0003	380	0.0112
Cl^- *	9600	10100	0.47	0.004	0.60	0.01	0.53	0.03	0.59	0.01	19000	0.56
SO_4^{2-} *	3570	3660	0.172	0.002	0.045	0.001	0.075	0.016	0.053	0.005	2210	0.065
Br^- *	50	52	0.0024	0.0000	0.0016	0.0001	0.0017	0.0002	0.0005	0.0001	65	0.0019
HCO_3^-	590	660	620	50	nd	nd	260	240	50	60	142	
TDS	20600	21400	21000	600	8100	2800	24000	46000	84000	27000	34000	
Al	0	0	0	0.1	1.2	1.3	0.3	2.1	8	14	0.01	
Si	6	8	7	1	28	3	30	11	8	12	3	
V	0	0	0	0.005	nd	nd	nd	nd	nd	nd	0.002	
Cr	0.003	0	0.002	0.002	0.003	0.002	0.004	0.030	0.04	0.09	0.00005	
Mn	0.05	0.02	0.035	0.021	1.2	0.7	1	4	3	4	0.002	
Fe	0.14	0	0.07	0.10	0.7	0.3	3	10	0.5	1.4	0.01	
Co	0	0	0	0.005	0.012	0.006	0.01	0.04	0.19	0.19	0.0003	
Ni	0	0	0	0.01	0.01	0.01	0.01	0.05	0.26	0.27	0.005	
Cu	0.013	0	0.007	0.009	nd	nd	0.01	0.03	0.08	0.06	0.003	
Zn	0.025	0.005	0.015	0.014	nd	nd	0.06	0.20	0.3	0.8	0.01	
As	0.22	0	0.11	0.15	nd	nd	0	0.3	0.04	0.30	0.003	
Sr	6	5.7	5.9	0.2	1.6	0.5	2.4	2.7	7	4	8	
Ag	0.002	0.003	0.003	0.002	nd	nd	0.005	0.030	0.02	0.03	0.0003	
Cd	0.013	0.004	0.009	0.006	nd	nd	0.004	0.014	0	0.005	0.0001	
Sb	0.32	0.01	0.17	0.22	nd	nd	0.00	0.02	0	0.02	0.0003	
I^-	2.6	1.6	2.1	0.7	0.05	0.06	0.5	0.9	0.5	0.4	0.06	
Ba	0.018	0.002	0.010	0.011	0.053	0.004	0.06	0.12	0	0.01	0.03	
Hg	0	0	0	0.002	nd	nd	nd	nd	nd	nd	0.00003	
Pb	0	0.01	0.005	0.007	nd	nd	0.13	0.28	0	0.05	0.00003	
Bi	0	0	0	0.003	nd	nd	0	0.25	0.06	0.25	0.00002	
Au	0.012	1.01	0.5	0.7	nd	nd	0.13	0.21	0.3	0.6	0.01	

All concentrations in mg/L, except Au in µg/L unless otherwise noted.

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

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

* - For the elements Na, Mg, Ca, K, Cl^-, SO_4^{2-} and Br^-, the mean and standard deviation apply to the ratio of the element concentration divided by TDS.
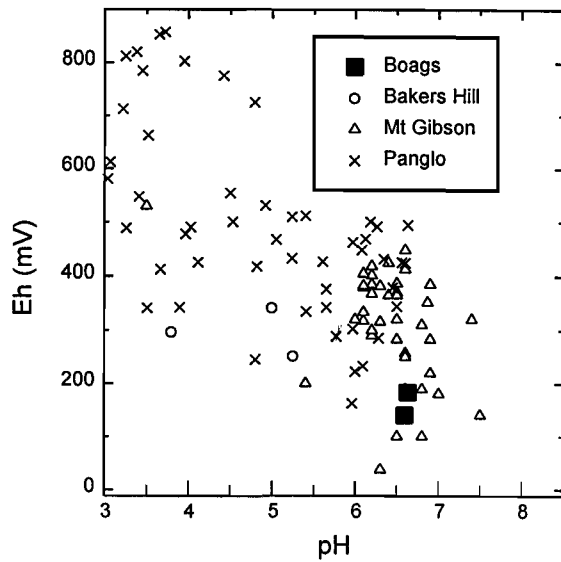
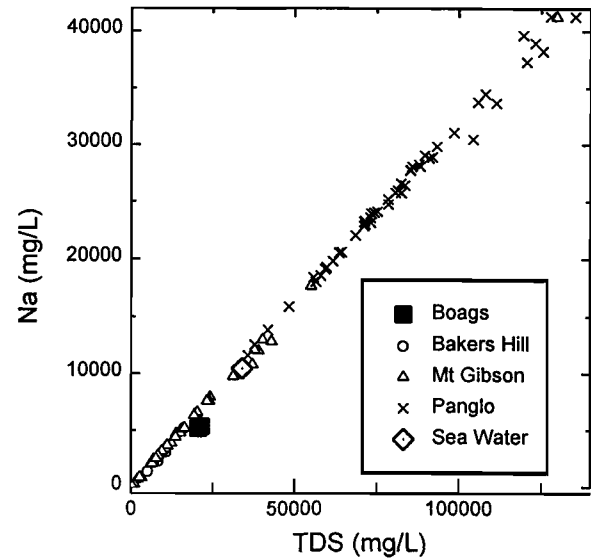nd - not determined

Figure 1: Eh vs. pH for water samples.

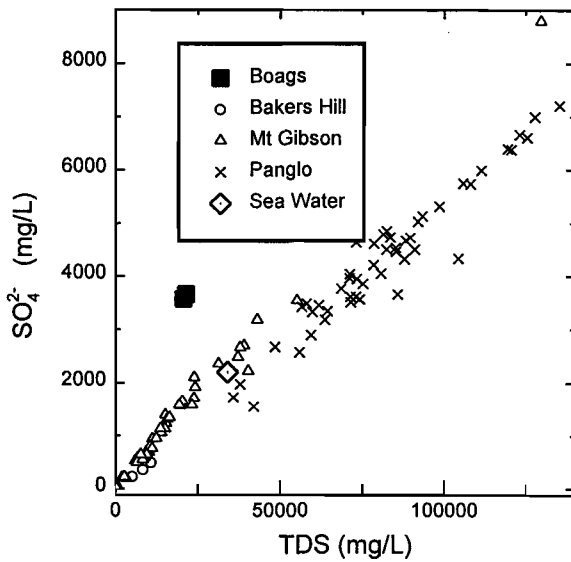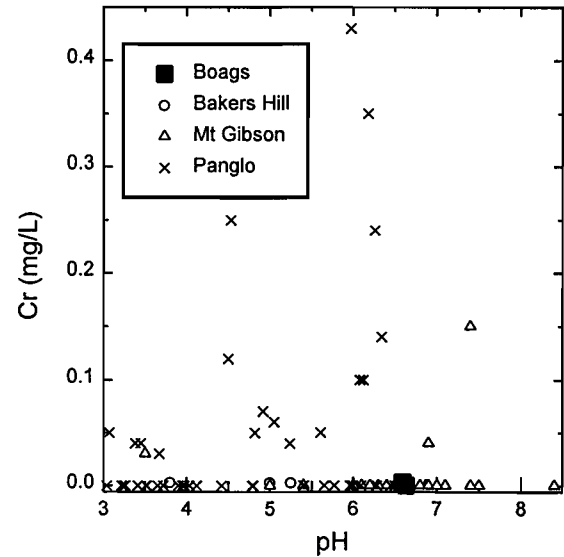Figure 2: Na vs. TDS for water samples.

Figure 3: SO_4^{2-} vs. TDS for water samples.
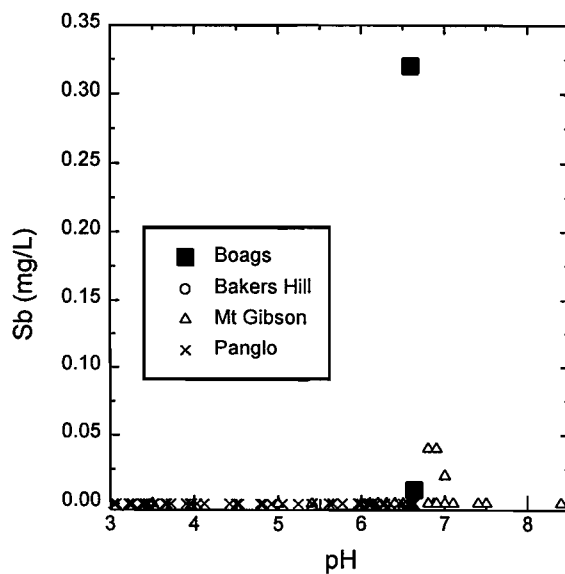

Figure 4: Cr vs. pH for water samples.
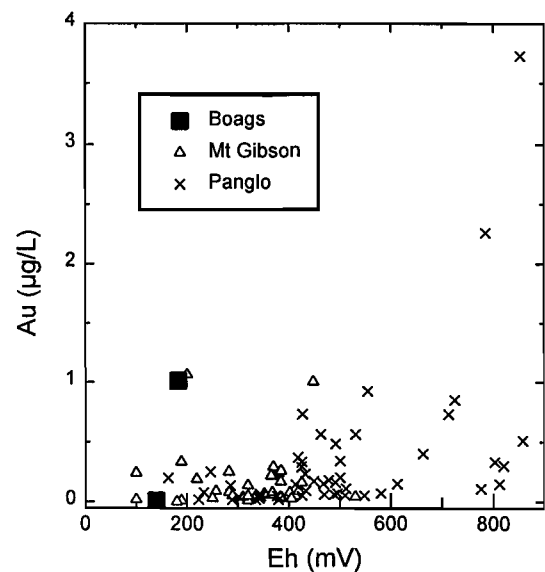

Figure 5: Sb vs. pH for water samples.

Figure 6: Au vs. Eh for water samples.

In Table 1, the results for the elements Na[1], Mg, Ca, K, Cl⁻, SO_4^{2-} and Br⁻ are given both as the absolute concentrations (columns 2 and 3 for Boags and column 12 for sea water) and, more usefully, as the ratio over TDS [columns 4 (Boags), 6 (Bakers Hill), 8 (Mt. Gibson), 10 (Panglo) and 13 (sea water)], hereafter described as the TDS ratio. The rationale for the use of TDS ratios is demonstrated in Figure 2, which shows Na concentration plotted vs TDS. As observed, the two are closely correlated, suggesting that all of the waters have arisen from dilution or evaporation of sea water. If this is the case, then the TDS ratios of the various elements for samples at the various sites should be the same as for sea water. This is generally the case for Bakers Hill and Mount Gibson (Table 1), while Panglo appears to be enriched in Na and Cl and depleted in the other major elements, possibly due to dissolution of halite (NaCl) at the site (Gray, 1990). The Boags waters show significant deviations from the sea water TDS ratios, being depleted in Na, K and Cl⁻, and enriched in Mg and Ca (possibly from carbonate dissolution; Eqn. 2), SO_4^{2-} (possibly from sulphide oxidation; Eqn. 1) and Br⁻. The particularly strong enrichment of SO_4^{2-} in the Boags samples is illustrated in Figure 3.

Analysis of the minor element contents (Table 1) shows some distinctive characteristics. The Al concentration in groundwater is controlled by the pH (Gray, 1990, 1991) and in waters with pH > 5.0, such as at Boags, Al concentration is below the detection limit. Silicon concentration is controlled by lithology, pH and salinity and the Boags waters have comparable Si contents to the other sites. Concentrations of Cr (Fig. 4) and other transition metals and Pb are low, partially as a consequence of the neutral pH conditions. Strontium is correlated with Ca, while Ba has concentrations comparable with the other sites.

The Boags waters have highly anomalous concentrations of As, Cd, Sb (Fig. 5), I⁻ and Au (Fig. 6). The As, Cd and Sb may all arise from the initial weathering of sulphides and arsenides. Levels of the elements is generally lower in surface waters at the other sites, suggesting other reactions removing them from solution (Section 4). High I⁻ levels observed at Boags (35 times higher than sea water; Table 1), correlate with observations at Mt Gibson and Panglo (Gray, 1990, 1991), indicating the enrichment of I within mineralized areas. Use of the halides F, Cl and Br for detection of mineralization is well documented (Frick *et al.*, 1989 and references given therein). Work has suggested that I is a chalcophile element (Fuge and Johnson, 1984, 1986), extensively enriched in sulphide environments (Chitayeva *et al.*, 1971; Fuge *et al.*, 1988) and that it may be a useful pathfinder for mineralization (Xuejing *et al.*, 1981; Andrews *et al.*, 1984; Fuge *et al.*, 1986).

The dissolved Au values (up to 1 µg/L) in the Boags samples are highly anomalous. Due to the low levels of Au it is not possible to directly determine the chemical form of the dissolved Au. On the basis of previous work (Gray, 1988 and references given therein) the most likely forms are either as the chloride complex ($AuCl_2^-$) or the thiosulphate complex [$Au(S_2O_3)_2^{3-}$]. A plot of Au vs. Eh (Fig. 6) shows that at Panglo, in particular, there is a general correlation between Au content and Eh, with the very oxidized waters (Eh ≈ 800 mV) having the highest Au concentration. This is consistent with Au being mobilized as the chloride complex at Panglo (Gray, 1990). Boags (and, to some degree, Mount Gibson) differs in that the sample with the high Au concentration has a low Eh, suggesting that in this case Au is present as

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[1] Note that in general elements will be denoted purely by symbol, without valence information: *i.e.* Na rather than Na⁺, with the exception of HCO_3^-, SO_4^{2-}, Cl⁻ and Br⁻, which were analysed as the anions.

$Au(S_2O_3)_2^{3-}$. However, the $S_2O_3^{2-}$ concentration (analysed as the free ion) was below the detection limit in both samples. This result is not absolutely inconsistent with the presence of $Au(S_2O_3)_2^{3-}$, as the Au complex could be formed at the interface where sulphides are weathering (and forming $S_2O_3^{2-}$) and Au is being dissolved. Because of the strength of the Au^+- $S_2O_3^{2-}$ bond the $Au(S_2O_3)_2^{3-}$ complex can then act to mobilize the Au and stabilize the $S_2O_3^{2-}$ ligand: *i.e.*, $Au(S_2O_3)_2^{3-}$ is more stable than $S_2O_3^{2-}$ alone.

4. Speciation Analysis

The speciation of the analysed elements, and their potential solid phases, was investigated using the speciation programme PHREEQE (Parkhurst *et al.,* 1980). This program, and the data derived from it, are described in detail in Gray (1990) and Gray (1991). For the purposes of this discussion, only the solubility index (SI) parameter, which is calculated for a number of mineral phase for each water sample, is considered. If the SI parameter <u>equals zero</u> (empirically from -0.5 to 0.5) the water is in <u>equilibrium</u> with the solid phase, under the conditions specified. Where the SI is <u>less than zero</u> (say < -0.5), the solution is <u>under-saturated</u> with respect to the phase, so that, if present, the phase may dissolve. If the SI is <u>greater than zero</u> (say > 0.5) the solution is <u>over-saturated</u> with respect to this phase and the phase can precipitate. Note that this analysis only specifies <u>possible</u> 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 speed of solution equilibration with this mineral (Drever, 1982).

The SI for a number of relevant phases (generally the least soluble mineral phase for each element tested) are shown in Table 2 and graphically for selected minerals in Figs. 7 - 10. The SI data for particular minerals are discussed below, in terms of the cations involved.

The SI for *calcite* plotted against pH for samples from all four sites is shown on Figure 7. The SI increases with pH, due to HCO_3^- converting to CO_3^{2-} (which then reacts with Ca^{2+} to form calcite) at higher pH, until reaching equilibrium levels close to neutrality. The Boags waters lie very close to the equilibrium line (the dotted line for SI = 0), indicating solution equilibrium with this phase. Similarly, the Boags waters appear to be in equilibrium with *magnesite* (Table 2), again indicating active carbonate equilibration. Conversely, when Ca is dissolved during carbonate dissolution (Eqn. 2) and SO_4^{2-} is produced during sulphide oxidation (Eqn. 1) enough Ca and SO_4^{2-} can be present for the water to reach *gypsum* saturation, as observed for Boags (Fig. 8). Note that Boags samples reached gypsum saturation at much lower TDS values than for the other sites, due to their relatively higher levels of Ca and SO_4^{2-}.

Other solid phases that appear to be in equilibrium with the Boags groundwater are *barite*, controlling Ba concentration, and *quartz*, controlling Si concentration. The Boags waters are undersaturated with respect to the solid phases of most of the other elements, indicating that they are being removed from solution by other processes (*e.g.*, adsorption) or that they are being dissolved very slowly. One exception to this is Sb, which is strongly oversaturated with respect to the solid phase *Sb(OH)₃* (Fig. 9). One explanation for this effect is that Sb is being released via oxidation reactions involving sulphides or arsenides containing reduced Sb. This released Sb

is highly anomalous (Fig. 5) and with time Sb would be expected to reprecipitate, either as $Sb(OH)_3$ or via other mechanisms. Thus, the high Sb concentration observed for Boags North is highly localized and should not be generally observed, consistent with observations described here. The Mt. Gibson waters with high Sb were sampled at depth from Tobias' Find, which is a Au-containing sulphide body (Anand *et al.*, 1989) in contact with neutral groundwater (Gray, 1991). Down-gradient from Tobias' Find Sb concentrations in the groundwater were below detection, consistent with the hypothesis that high Sb concentration is restricted to areas of sulphide weathering.

Table 2: Saturation Indices (SI's) of Boags Pit waters for various minerals.

| Mineral | Formula | Boags | |
		North	South
Calcite	$CaCO_3$	0.08	0.17
Gypsum	$CaSO_4.2H_2O$	-0.24	-0.23
Dolomite	$MgCa(CO_3)_2$	0.76	0.93
Magnesite	$MgCO_3$	0.09	0.17
Celestine	$SrSO_4$	-0.59	-0.61
Barite	$BaSO_4$	-0.06	-1.01
Halite	$NaCl$	-3.16	-3.12
Quartz	SiO_2	0.29	0.43
Amorphous Silica	SiO_2	-0.97	-0.83
Ferrihydrite	$Fe(OH)_3$	-1.05	-
Rhodocrosite	$MnCO_3$	-1.69	-2.01
Manganite	$MnOOH$	-10.03	-9.59
Atacamite	$Cu_2Cl(OH)_3$	-11.12	-
Smithsonite	$ZnCO_3$	-3.16	-3.77
Otavite	$CdCO_3$	-0.81	-1.26
Cerrusite	$PbCO_3$	-2.25	-1.37
$PbClO_5(OH)_{1.5}$	$PbClO_5(OH)_{1.5}$	-3.88	-3.03
Iodyrite	AgI	-0.71	-
Au Metal	Au	6.53	8.15
$Sb(OH)_3$	$Sb(OH)_3$	1.56	0.05

The speciation data used to derive the SI values for *Au metal* (the important solid phase of Au) only included the concentration of ligands such as chloride or iodide (as thiosulphate was, in many cases, below detection). This results in the calculated SI for Au metal being dominantly controlled by Eh (Fig. 10). Indeed, the highly oxidized waters (Eh > 650 V) are theoretically significantly undersaturated with respect to Au metal. However, any determination of the theoretical solubility of Au is questionable, given the major effect of ligands such as $S_2O_3^{2-}$, even when at concentrations below the detection limit (Gray, 1991), and also kinetic factors such as an enhanced stability of $S_2O_3^{2-}$ when bonded to Au. Given the absence of data, the effect of thiosulphate cannot presently be properly tested.
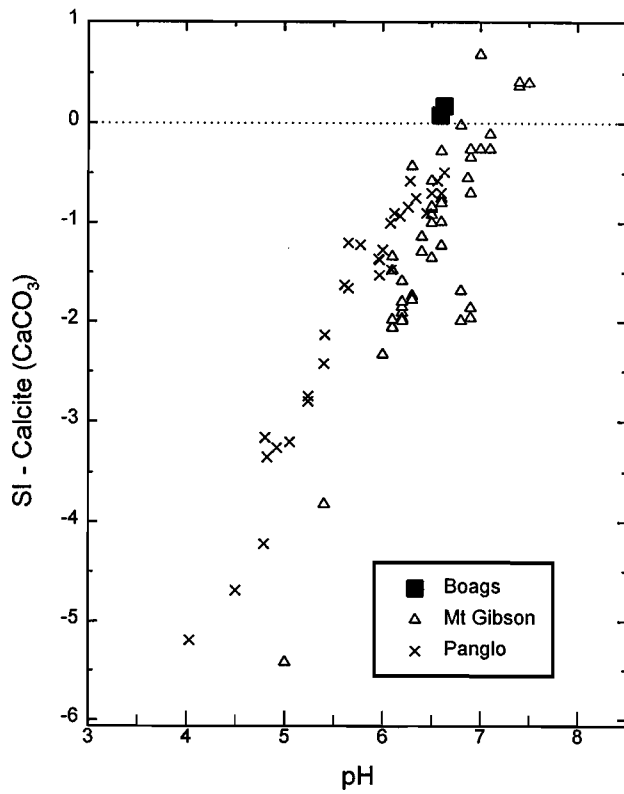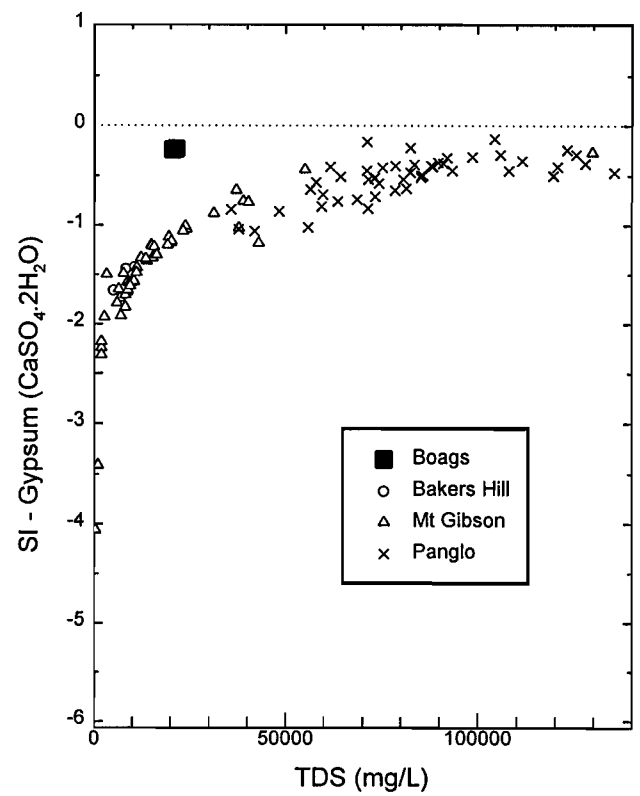
Figure 7: SI for Calcite vs. pH.

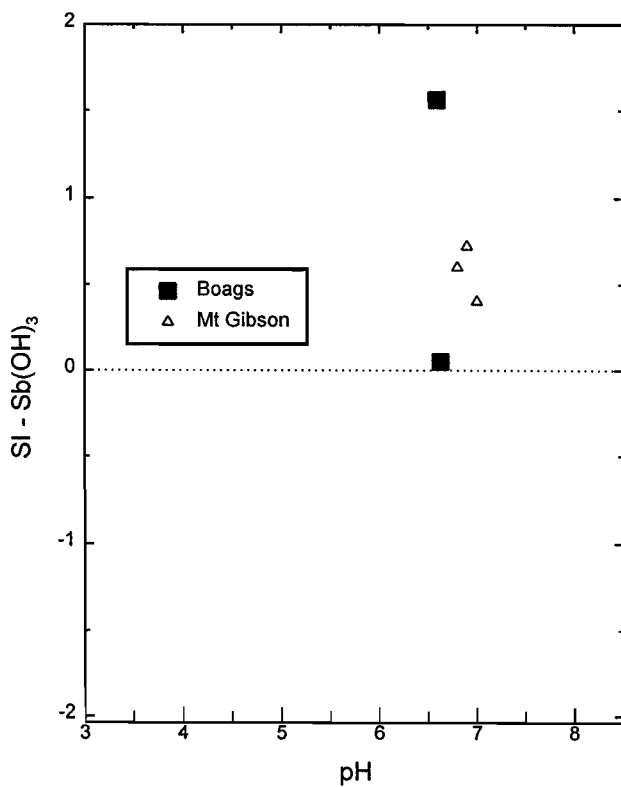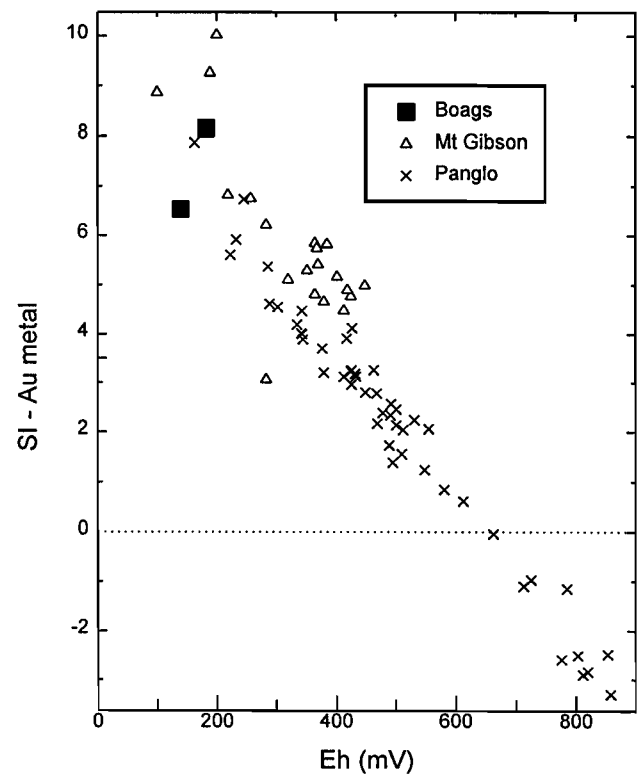Figure 8: SI for Gypsum vs. TDS.

Figure 9: SI for Sb(OH)$_3$ vs. pH.

Figure 10: SI for Au metal vs. Eh.

This effect of ligands at or below detection is nowhere near as pronounced for the other elements investigated, as the strength of bonding with ligands such as $S_2O_3^{2-}$ with the other metals analysed is much weaker than for Au, and major constituents such as Cl^-, HCO_3^- or OH^- will be more important for complexation and solubilization. That is, the conclusions on the other elements (apart from Au) would not be invalidated by assuming the presence of ligands such as $S_2O_3^{2-}$ at levels below detection.

5. General Discussion

The elements that are anomalously enriched in the groundwaters from Boags, and their possible sources, are:

(i) Ca, Mg and HCO_3^-, derived from dissolution of carbonate minerals (Eqn. 2);

(ii) SO_4^{2-}, As, Cd and Sb, released during oxidation of sulphide (Eqn. 1), arsenide and/or antimonide minerals;

(iii) I^- and (possibly) Br^-, which have been observed to be extensively enriched in sulphide environments (Chitayeva et al., 1971; Fuge et al., 1988; Gray, 1990, 1991);

(iv) Au, dissolved as the $S_2O_3^{2-}$ complex, as $S_2O_3^{2-}$ is released during neutral oxidation of sulphide (Eqn. 3).

If analogous effects are present at other sites and extend laterally, they may present targets for hydrogeochemical exploration. The elements Ca, Mg, HCO_3^-, SO_4^{2-} and Br^- are present in the saline groundwater and concentrations will be reduced via dilution. In addition, Ca, HCO_3^- and SO_4^{2-} can be removed from solution by precipitation of calcite and gypsum, or, under acid conditions, as Al sulphates (Gray, 1990); and HCO_3^- can be lost as CO_2 gas if the waters become acidified. At Mount Gibson and Panglo (Gray, 1990, 1991) enrichment of Mg, SO_4^{2-} and Br^- can be observed adjacent to mineralization under some circumstances. However, the effects tend to be subtle and can be obscured for the reasons described above, and are therefore not easily observed.

Dissolved As, Cd and Sb concentration may be reduced by reactions such as precipitation or adsorption. The high Sb content of the Boags North water represents highly oversaturated conditions with respect to the solid phase $Sb(OH)_3$, and this Sb groundwater anomaly is thus expected to be highly localized. Iodide is, however, generally highly soluble, with the major loss from solution being via oxidation to I_2 (Fuge, 1990). This reaction is expected to be slow and, given the low background of I^-, the I^- anomaly is expected to only be slowly diluted and is commonly observed in mineralized areas (Gray, 1990, 1991).

The extent of the Au anomaly is highly dependant on solution conditions. If conditions remain neutral or only weakly acidic then the $Au(S_2O_3)_2^{3-}$ complex may have a moderate mobility, as observed at Mount Gibson, at the Midway deposit (Gray, 1991). However, if the waters are Fe-rich then oxidation in the upper part of the regolith can lead to waters with pH values down to 3. Under such conditions $Au(S_2O_3)_2^{3-}$ will be destabilized and Au precipitated. If conditions are sufficiently oxidizing, then Au may dissolve as the chloride complex, as

observed at Panglo. However, this is a secondary reaction, which is not direct related to the initial sulphide weathering reactions observed at Boags.

In general, if acidic conditions do occur then secondary dissolution of a whole series of elements is observed, particularly of the transition metals Cr, Mn, Co, Ni, Cu and Zn. This phenomenon was observed at Panglo (Gray, 1990), and to a lesser extent, downgradient from the sulphide body at Midway, Mount Gibson (Gray, 1991), where acid groundwater conditions occur due to oxidation and hydrolysis of Fe (Eqn. 4). This effect is less localized than neutral sulphide weathering reactions, as described for Boags, and tends more to distinguish lithological domains (Gray, 1990) rather than pin-pointing mineralization.

In summary, results from Boags suggest that specific elements may be released at anomalous and detectable levels during neutral sulphide weathering, due to reactions described in Sections 3 and 4. Anomalous levels of some of these elements may be maintained as waters disperse, depending on groundwater conditions. The most extensive anomaly appears to be that of greater I⁻ content.

Acknowledgements

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