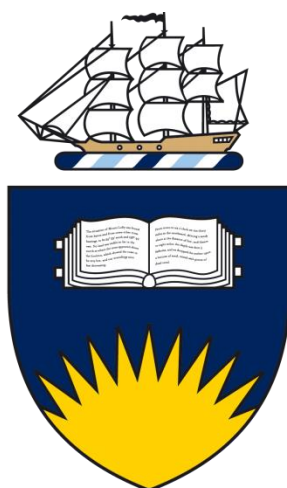


The Speciation of Gold in Mine Wastes and Natural Waters

A thesis submitted for fulfilment of the degree of
Doctor of Philosophy

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3. Application to water samples

3.1 Introduction

The determination of gold in groundwaters is an emerging technique in the field of mineral exploration [157]. The analysis of such waters reduces the heavy reliance on costly drilling programs to identify target areas. The time-consuming process of analysing a narrow cylinder of rock that represents a small area, is replaced with the analysis of series of groundwater samples that provide information about a larger geological area. The concentration of gold in groundwaters are determined by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry), and has been used as pathfinder for gold mineralisation [103, 157]. These methods characterise the total gold concentration, and do not give information about the speciation. The ability to speciate gold will provide additional information about the geological conditions under which gold is mobilised. In addition it will be useful for understanding bioremediation processes and such knowledge could also influence the choice and concentration of lixiviant used in gold leaching.

In this chapter we examined sixty two water samples associated with gold mines (i.e. process water, tailings dam, environmental monitoring bores), and groundwaters samples collected from bores around Australia. Au(I)-thiosulfate was expected near sulfide-rich mineralised areas (i.e. Fifield, Lake Way) and Au(I)-cyanide was expected to be found in the mine tailings and process waters as cyanide is a common lixiviant in gold leaching (the presence of Au(I)-cyanide has been predicted in models of waters near mining processes where possible leaching has occurred [94]). Samples from acidic brines were not collected, so Au(III) halides were not expected. $[\text{Au}(\text{Cl})_4]^-$ is not stable unless in acidic and very oxidising conditions, as shown in Figure 3-1, a speciation plot of gold with various species (at concentrations typical of groundwaters conditions), at a sliding fugacity and pH scale. Instead the majority of the species are Au(I)-Cl-OH complexes, and Au(I) sulfide species at very reducing conditions. However our method did not include these Au(I) species, because there were no readily soluble standards available.

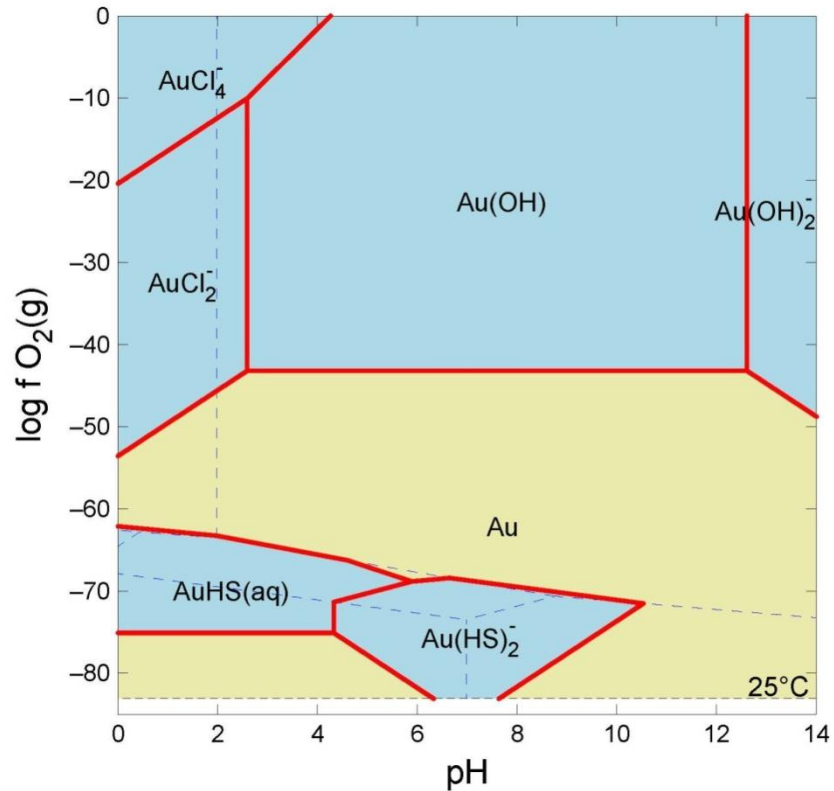


Figure 3-1 Log fO_2 -pH speciation plot of Au in the presence of various common ligands.
 $a[Au^+] = 10^{-12}$, $a[H_2O] = 1$, $a[Cl^-] = 1$, $a[CN^-] = 10^{-54}$, $a[Br^-] = 10^{-6}$, $a[SO_4^{2-}] = 10^{-3}$.
 Suppressed: $[AuCl_3]^{2-}$.

3.2 Study Scope

Presented in this chapter is the application of the developed speciation method to $[Au(CN)_2]^-$ determination in mine waters, and the identification of Au(III) species in a groundwater sample. The unexpected detection of Au(III) species in several groundwater is further investigated in Chapter 4, which presents preliminary studies into the oxidation of Au(I) or Au(0) to Au(III) by manganese compounds.

3.3 Experimental

3.3.1 Reagents and Standards

The chemicals used in this study are shown in Table 3-1. Unless otherwise specified ~18 MΩcm deionised water (Millipore, Australia) utilised for the preparation of aqueous solutions.

Table 3-1 The chemicals used in this study.

Chemical	Supplier	Grade	Concentration/Purity
Acetonitrile	Ajax Finechem	HPLC	99.7%
Agilent ICP-MS stock tuning solution (Ce, Co, Li, Tl, Y)	Agilent Technologies	Analytical	10 mg L ⁻¹
Disodium orthophosphate phosphate anhydrous powder	Scharlau	Analytical	>99.0%
Gold Standard in 2% HCl	Choice Analytical	Analytical	1000 mg L ⁻¹
Gold Standard in 5% HCl	Sigma Aldrich	Analytical	1001 + 2 mg L ⁻¹
Hexadecyltrimethylammonium hydroxide solution (HDTMAOH)	Sigma-Aldrich	Reagent	10 wt. % in H ₂ O
High Purity HCl	Scharlau	Analytical	37%
Isopropanol	Merck	HPLC	Not stated
Orthophosphoric acid	Ajax Finechem	Analytical	85%
Potassium cyanide	Scharlau	Reagent	Not stated
Potassium gold(I) cyanide	Strem Chemicals	Reagent	99%
Sodium dihydrogen phosphate anhydrous	Chem-Supply	Analytical	>98%
Sodium Hydroxide	Ajax Finechem	Analytical	>99%
Tetrabutylammonium chloride hydrate (TBAC)	Sigma-Aldrich	Reagent	98%
Triton™ X-100	Sigma-Aldrich	Analytical	100%

3.3.2 Water samples

Sampling method

Water samples were obtained from a number of gold mining sites, environmental bores and groundwaters in Australia, as listed in Table 3-4. These samples were collected over several field trips by different people/organisations. When available onsite water pumps were used to extract waters, otherwise plastic PVC bailers were lowered into the bore. The Fifield samples were collected from the first flush in the Bore 1 and 3 as well as two hours after pumping of the Bore 1. The samples were frozen immediately after collection in acid washed 1 L plastic (Silverlock Packaging, Australia) and 50 mL plastic (Falcon, BD Biosciences) tubes and stored in the freezer at -20 °C. The water samples were brought to room temperature before analysis.

Table 3-2 List of water samples collected for this study.*Samples collected by Dr. Frank Reith, Dr. Joël Brugger and Dr. Carla Zammit.**Samples collected by ¹ Dr. Susan Wilson and ² PIRSA as indicated.*

Sites	Location	Sampling Date
Black Lode ¹	30° 57' 33" S, 152° 27' 52" E	28/06/2011
Elenora ¹	30° 34' 33" S, 151° 53' 58" E	28/06/2011
Fifield Bore 1	N.S.W.	32° 49' 27" S, 147° 28' 32" E
Fifield Bore 3		32° 49' 27" S, 147° 28' 32" E
Hillgrove capped tailings dam ¹	30° 34' 35" S, 151° 54' 35" E	28/06/2011
Sunlight mine ¹	30° 34' 50" S, 151° 53' 10" E	28/06/2011
Oberon	20° 17' 17" S, 129° 59' 14" E	01/12/2012
Old Pirate Bore 19	N.T.	20° 11' 11" S, 129° 09' 33" E
Old Pirate Noel Bore		20° 11' 35" S, 129° 07' 37" E
Tanami Granite Bore by Tailings	20° 32' 35" S, 130° 19' 33" E	01/12/2012
Kilkivan	QLD.	26° 05' 06" S, 152° 11' 47" E
#8 Bore ²	30° 11' 41" S, 136° 09' 50" E	04/03/2010
8 Mile Bore ²	29° 05' 38" S, 134° 36' 38" E	23/02/2012
Birthday Bore ²	30° 13' 09" S, 135° 50' 20" E	21/02/2012
Challenger Gold Mine (Gusher Bore)	29° 39' 49" S, 132° 42' 43" E	23/09/2010
Challenger Gold Mine (Processing Water)	29° 39' 49" S, 132° 42' 43" E	23/09/2010
Challenger Gold Mine (tailings)	29° 39' 49" S, 132° 42' 43" E	23/09/2010
Cheadle Bore ²	30° 19' 51" S, 135° 20' 00" E	19/01/2012
Claypan Bore ²	30° 01' 01" S, 136° 36' 02" E	18/02/2012
Clements Bore ²	30° 34' 25" S, 135° 53' 03" E	11/01/2012
Elliston Council Bore ²	33° 39' 00" S, 134° 53' 15" E	16/03/2012
Uley/Lincoln Basin USBP 1 ²	34° 45' 44" S, 135° 33' 31" E	22/03/2012
Coffin Bay Golf Club Bore ²	S.A.	34° 38' 03" S, 135° 28' 33" E
Heal's Bore ²	29° 57' 05" S, 135° 46' 54" E	22/02/2012
Homestead Well ²	30° 24' 23" S, 136° 24' 04" E	15/02/2012
Hope Bay Well ²	34° 08' 32" S, 135° 18' 23" E	18/03/2012
Hillview House Well ²	33° 54' 41" S, 135° 15' 41" E	17/03/2012
Knoll Bore ²	30° 52' 02" S, 136° 24' 34" E	16/02/2012
Lincoln Basin Obs# LNC 15 ²	34° 48' 31" S, 135° 45' 54" E	23/03/2012
Little Swamp Bore ²	31° 17' 58" S, 135° 24' 31" E	12/01/2012
Lochs Well ²	30° 39' 31" S, 136° 03' 21" E	14/02/2012
Mt. Cora Well ²	33° 57' 31" S, 135° 34' 14" E	19/03/2012
Mt. Eba House Bore ²	30° 10' 57" S, 135° 40' 04" E	17/02/2012
Mt. Vivian House Well ²	30° 35' 48" S, 135° 42' 17" E	10/01/2012
North Well ²	31° 12' 10" S, 135° 15' 29" E	13/01/2012
Orwell Well ²	30° 31' 29" S, 135° 35' 30" E	16/01/2012

Uley/Wanilla Basin Obs# WNL48 ²	S.A.	34° 36' 39" S, 135° 37' 38" E	21/03/2012
Wheepool Well ²		31° 39' 08" S, 135° 21' 31" E	13/01/2012
Ballarat		37° 33.239' S, 143° 50.104' E	04/10/2010
Coopers Creek upper adit		37° 59' 09" S, 146° 25' 35" E	06/10/2010
Creswick	VIC.	37° 25' 24" S, 143° 53' 38" E	07/10/2010
Maldon		37° 00' 07" S, 144° 04' 22" E	07/10/2010
Walhalla Empress Tunnel		37° 56' 49" S, 146° 26' 56" E	05/10/2010
Walhalla Long Tunnel		37° 55' 58" S, 146° 26' 56" E	05/10/2010
Agnew 34		27° 58' 42" S, 120° 29' 38" E	20/11/2012
Agnew Bore 27		27° 58' 42" S, 120° 29' 38" E	20/11/2012
Boddington 1		32° 45' 08" S, 116° 21' 19" E	26/11/2012
Boddington 2		32° 45' 08" S, 116° 21' 19" E	26/11/2012
British King		27° 56' 23" S, 121° 14' 35" E	22/11/2012
Contact hump/whaleback		28° 03' 06" S, 120° 32' 39" E	16/11/2012
Darlot Batterie		27° 56' 29" S, 121° 18' 25" E	22/11/2012
Jundee 1		26° 21' 04" S, 120° 35' 00" E	21/11/2012
Jundee 2	W.A.	26° 21' 28" S, 120° 35' 41" E	21/11/2012
KCGM		30° 46' 43" S, 121° 30' 14" E	24/11/2012
Knobbies 1		28° 18' 31" S, 118° 00' 57" E	19/11/2012
Knobbies 2		28° 18' 31" S, 118° 00' 57" E	19/11/2012
Lake Way		26° 45' 32" S, 120° 16' 56" E	16/11/2012
Plutonic West 1		25° 18' 38" S, 119° 26' 44" E	21/11/2012
Plutonic West 2		25° 18' 38" S, 119° 26' 44" E	21/11/2012
Wildara		28° 08' 21" S, 120° 49' 48" E	18/11/2012
Wildcat Working 1		28° 02' 04" S, 120° 31' 24" E	18/11/2012
Wildcat Working 2		28° 02' 05" S, 120° 31' 27" E	18/11/2012

Total Au concentration with ICP-MS

Samples were quantified via standard additions (to account for any matrix effects) of Au(III)-chloride (from a 1000 mg L⁻¹ Au stock in 5 % HCl). The standard additions were prepared gravimetrically to an approximate weight of 5 g and 10% wt. HCl. The solutions were left overnight to allow the gold speciation to equilibrate, before being syringe-filtered (PDVF, 0.45 µm) and analysed.

HPLC-ICP-MS speciation analysis

The water samples were brought to room temperature and syringe-filtered (PDVF, 0.45 µm) before direct analysis on the HPLC-ICP-MS (the procedure is described in the previous chapter).

Quantification with HPLC-ICP-MS

Samples were quantified by multiple standard addition of potassium gold(I) cyanide with HPLC-ICP-MS. The level of [Au(CN)₂] was quantified via a multiple standard additions

method where solutions were prepared gravimetrically with successive standard additions of potassium gold(I)-cyanide to the sample matrix. The uncertainty in the concentration was calculated by taking into account the error of the slope and the error of the y-intercept. For the spike-and-recovery analysis a spiked bore water sample (Granites Gold Mine) was prepared containing a $7 \mu\text{g L}^{-1}$ $[\text{Au}(\text{CN})_2]^-$ spike. Four successive standard additions of $4 \mu\text{g L}^{-1}$ and $8 \mu\text{g L}^{-1}$ of $[\text{Au}(\text{CN})_2]^-$ were added to the unspiked and spiked samples respectively.

Cyanide measurements

0.3256 g of potassium cyanide (Scharlau, Spain) was dissolved in a sodium hydroxide solution (50 ml, pH 12) to form a 0.1 M CN^- stock solution. 0.1, 0.3, 0.5, 1, 2, 5, 8, 10, 26, 260, 2600 ppm CN^- standards (5×10^{-6} M to 0.1 M) were made from appropriate dilutions of the stock. The water samples were adjusted to pH 12 with a concentrated NaOH solution. The cyanide ion concentrations were determined by a TPS uniProbe Cyanide ISE (TPS Pty Ltd, Australia). Samples and standards were stirred with a magnetic stirrer bar during measurement.

3.3.3 ICP-MS set up

Total Au was measured with an Agilent 7500cx ICP-MS. During analysis the sample and In internal standard was introduced into the concentric nebulizer (0.4 mL min^{-1}) by means of a tee splitter. Operating conditions for the ICP-MS are given in Table 3-3. In all cases, the ICP-MS was tuned with a $1 \mu\text{g L}^{-1}$ (Ce, Co, Li, Tl, Y) tune solution (Agilent Technologies, U.S.) made up in 2% nitric acid. Nickel cones and a 2.5 mm ID diameter torch was used.

Table 3-3 ICP-MS operating conditions and data acquisition parameters

ICP-MS	Agilent 7500cx
Forward Power	1500 W
Plasma gas flow	Ar, 15 L min^{-1}
Auxillary gas flow	Ar, 0.9 L min^{-1}
Nebulizer gas flow	Ar, 1.02 L min^{-1}
He gas flow	4.5 mL min^{-1}
Octapole bias	-20 V
QP bias	-16 V
Torch sampling depth	10 mm
Masses monitored	Au^{197} , In^{115}
Acquisition mode	Spectrum
Detection	Electron multiplier (pulse mode voltage 1070 V)
Integration time/mass	0.1 s
Replicates	5
Peripump rate	0.1 rps
Spray chamber	2°C

3.3.4 ICP-MS procedure

After lighting the ICP-MS plasma and allowing it to stabilise for half an hour, the autotune program was used to set the ICP-MS parameters. This was done by introducing the $1 \mu\text{g L}^{-1}$ Ce, Co, Li, Tl and Y tune solution (Agilent Technologies, U.S.) into the ICP-MS through tygon peristaltic pump tubing (ID 1.02 mm, Ismatec, Switzerland) at a rate of 0.1 rps. Between each sample a rinse program was employed to wash out the residual gold: 10% vol. HCl (twice) and then water for 15 seconds each. Raw data was initially recorded using the Agilent MassHunter Workstation Software, then extracted into OriginPro v. 7.5 for analysis and presentation purposes.

3.3.5 Water composition analysis

All water analyses were run by Julie Smith from the Analytical Chemistry Unit in CSIRO Land and Water, Waite. Water samples were analyzed for pH [167], electrical conductivity (APHA method 2510), and alkalinity (APHA method 2320). Dissolved carbon (DC) was determined by APHA method 5310 B on a Skalar Formacs HT TOC/TN Analyzer. Inorganic carbon was acidified to form CO_2 prior to detection. DOC (dissolved organic carbon) was determined by the difference between total carbon and inorganic carbon. Total nitrogen was determined at the same time as total carbon on the dual detector instrument. Ammonia-Nitrogen ($\text{NH}_4\text{-N}$) was determined by flow analysis and spectrometric detection according to ISO 11732. Nitrate- (and Nitrite-) Nitrogen was determined by APHA method 4500-NO₃-F using the automated segmented flow analyser (Alpkem Flow Solution 3) at 540 nm. The $\text{NO}_3\text{-N}$ (also referred to as $\text{NO}_x\text{-N}$ indicating the sum of nitrite and nitrate nitrogen) concentration is calculated from a set of calibration standards measured at the same time. Anions (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , SO_4^{2-} and PO_4^{3-}) were measured by the APHA method 4110 using a Dionex ICS-2500 ion chromatography system with 2 mm AS16 anion separation column. The cations and metals were determined by APHA method 3120 using inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Spectro ARCOS (Spectro Analytical Instruments, Kleve, Germany). Trace and ultratrace metals were analyzed (Table 3-8) by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500ce, USA).

3.3.6 Modelling Studies

Geochemist's Workbench software (RockWare®, USA) [125] was used to construct log-log activity gold speciation diagrams. Thermodynamic properties were taken from the Lawrence Livermore National Laboratory database (version R9), with properties for Au complexes from Usher *et al.* [84].

3.4 Results and Discussion

3.4.1 Determination of total Au by ICP-MS water samples

All water samples listed in Table 3-4 were first analysed with ICP-MS to determine the concentration of total gold. Then samples containing gold were analysed by HPLC-ICP-MS to determine the speciation of gold.

Table 3-4 Water samples analysed in this chapter.

Note: N.D. = not detected, *3 point calibration, **4 point calibration instead of 5, n = 1.

Sites	Location	Total [Au] ($\mu\text{g L}^{-1}$)	Au species detected by HPLC-ICP-MS
Black Lode		N.D.	N.D.
Elenora		N.D.	N.D.
Fifield Bore 1	N.S.W.	0.9 ± 0.3	Au(III)?
Fifield Bore 3		0.20 ± 0.06	Au(III)?
Hillgrove capped tailings dam		N.D.	–
Sunlight Gold Mine		0.06 ± 0.02	N.D.
Oberon		$0.17 \pm 0.01^*$	–
Old Pirate Bore 19	N.T.	N.D.	N.D.
Old Pirate Noel Bore		N.D.	N.D.
Tanami Granite Bore		13.5 ± 0.7	[Au(CN) ₂] ⁻
Kilkivan	QLD.	N.D.	–
#8 Bore		N.D.	N.D.
8 Mile Bore		N.D.	N.D.
Birthday Bore		N.D.	N.D.
Challenger Gold Mine (Gusher Bore)		N.D.	N.D.
Challenger Gold Mine (Processing Water)		1.9 ± 0.6	[Au(CN) ₂] ⁻
Challenger Gold Mine (tailings)	S.A.	1.3 ± 0.6	[Au(CN) ₂] ⁻
Cheadle Bore		N.D.	–
Claypan Bore		N.D.	N.D.
Clements Bore		N.D.	–
Elliston Council Bore		N.D.	N.D.
Uley/Lincoln Basin USPB 1		N.D.	N.D.
Coffin Bay Golf Club Bore		N.D.	N.D.
Heal's Bore		N.D.	N.D.
Homestead Well		N.D.	N.D.

Hope Bay Well		N.D.	N.D.
Hillview House Well		N.D.	N.D.
Knoll Bore		N.D.	N.D.
Lincoln Basin Obs# LNC 15		N.D.	N.D.
Little Swamp Bore		N.D.	–
Loch's Well		N.D.	N.D.
Mt. Cora Well	S.A.	N.D.	N.D.
Mt. Eba House Bore		N.D.	N.D.
Mt. Vivian House Well		N.D.	–
North Well		N.D.	–
Orwell Well		N.D.	–
Uley/Wanilla Basin Obs# WNL48		N.D.	N.D.
Wheepool Well		N.D.	–
Ballarat		N.D.	–
Coopers Creek upper adit		N.D.	–
Creswick	VIC.	N.D.	–
Maldon		N.D.	–
Walhalla Empress Tunnel		N.D.	–
Walhalla Long Tunnel		N.D.	–
Agnew 34		1.15 ± 0.01*	[Au(CN) ₂] ⁻
Agnew Bore 27		13 ± 2**	[Au(CN) ₂] ⁻
Boddington 1		0.8 ± 0.2*	[Au(CN) ₂] ⁻
Boddington 2		N.D.	–
British King		0.50 ± 0.08*	Au(III)?
Contact hump/whaleback		N.D.	–
Darlot Batterie		0.066 ± 0.007	–
Jundee 1		N.D.	–
Jundee 2		N.D.	–
KCMG	W.A.	N.D.	–
Knobbies 1		N.D.	–
Knobbies 2		N.D.	–
Lake Way		0.45 ± 0.04*	Au(I) and Au(III)
Plutonic West 1		N.D.*	–
Plutonic West 2		0.19 ± 0.01	N.D.
Wildara		0.12 ± 0.2	–
Wildcat Working 1		N.D.	N.D.
Wildcat Working 2		N.D.	–

3.4.2 Application to water samples associated with gold mines

Water samples from several sites were analysed with the developed HPLC-ICP-MS method. Three of these sites represent environmental monitoring bores near gold mines, whilst the fourth represents a dewatering pond in an open pit gold mine. The chromatograms reveal that $[\text{Au}(\text{CN})_2]^-$ was the only gold complex observed in the waters (Figure 3-2). $[\text{Au}(\text{CN})_2]^-$ was also detected in samples from two tailings dams and process water from a gold mine. These samples are shown on a separately in Figure 3-3, due to the intensity of the $[\text{Au}(\text{CN})_2]^-$ peak. The water samples in Figure 3-2 were quantified for $[\text{Au}(\text{CN})_2]^-$, via HPLC-ICP-MS. However the peak intensities of the samples in Figure 3-3 (~1600 – 2600 counts), appeared much too high for the total gold concentrations determine by ICP-MS ($\sim 1.3 \mu\text{g L}^{-1}$ – $1.9 \mu\text{g}^{-1}$). The possibility of elevated cyanide levels in these samples are investigated later. The peak at ~1.3 minutes is attributed to matrix effects as discussed in Section 0.

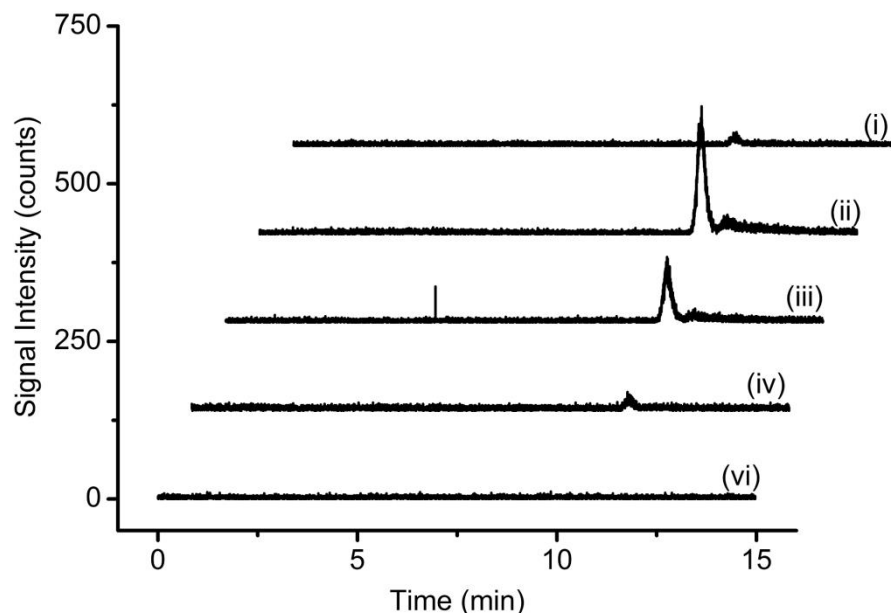


Figure 3-2 Detection of $[\text{Au}(\text{CN})_2]^-$ in water samples associated with gold mines.

Chromatograms show $[\text{Au}(\text{CN})_2]^-$ peak in water samples from monitoring bores: (i) Agnew 34, (ii) Agnew 27, and (iii) Tanami Granite, (iv) Boddington dewatering pond, and (v) Hillgrove tailings; Mobile phase: 6: 17.5 v/v isopropanol: acetonitrile, 1 mM TBAC, 5 mM $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$, pH 7.

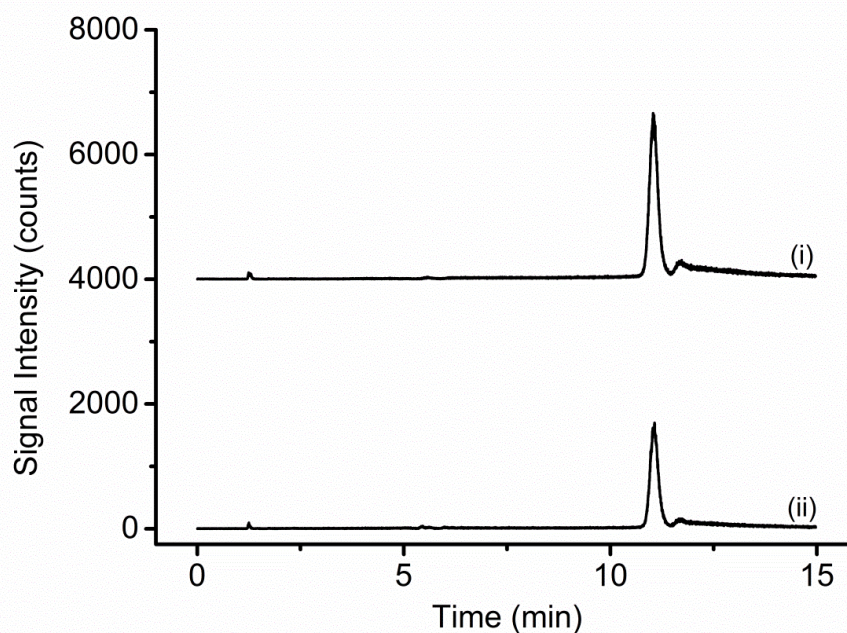


Figure 3-3 Detection of high $[\text{Au}(\text{CN})_2]^-$ signals in samples associated with gold mines. Chromatograms show $[\text{Au}(\text{CN})_2]^-$ peak in (i) tailings and (ii) processing waters from the Challenger Gold Mine; Other conditions as Figure 3-2.

Quantification of $[\text{Au}(\text{CN})_2]^-$

The concentration of $[\text{Au}(\text{CN})_2]^-$ in each sample was determined by multiple standard additions of a $\text{K}[\text{Au}(\text{CN})_2]$ standard with HPLC-ICP-MS. Matrix matching via standard additions was chosen for the analysis in order to allow for any suppression/enhancement of the signal that may result from other components in the sample matrix that may co-elute. As can be seen in Table 3-5, the concentrations of gold determined by HPLC-ICP-MS (approx. $0.5 \mu\text{g L}^{-1}$ to $8 \mu\text{g L}^{-1}$) were generally lower than the concentrations determined by ICP-MS (approx. $0.8 \mu\text{g L}^{-1}$ to $13 \mu\text{g L}^{-1}$). ICP-MS analysis was conducted months before HPLC-ICP-MS, so this difference in concentration may be due to the gradual adsorption of gold onto the walls of the bottles during the storage and repeated defrosting for analysis [168] (Section 4.1.1). These levels of Au correspond to $0.7 \mu\text{g L}^{-1}$ to $10.6 \mu\text{g L}^{-1}$ of Au(I)-cyanide. These levels of $[\text{Au}(\text{CN})_2]^-$ detected are well below the weak acid dissociable (WAD) cyanide concentrations deemed safe for wildlife (below 50mg L^{-1}) [169]. Furthermore $[\text{Au}(\text{CN})_2]^-$ is considered to be a strong acid dissociable complex, where only harsh acidic conditions will liberate free cyanide [170]. Thus, at these levels, $[\text{Au}(\text{CN})_2]^-$ should not pose an environmental risk for formation of free cyanide. The proximity of the bores to either tailings and the mine processes suggests that $[\text{Au}(\text{CN})_2]^-$ may result from mining processes, rather than cyanide producing plants or microorganisms. Further studies are required to verify the mechanism of formation and distribution of $[\text{Au}(\text{CN})_2]^-$ at these sites. The accuracy of the method was assessed by determining the recovery of $[\text{Au}(\text{CN})_2]^-$ in a spiked monitoring bore

water sample (from the Granites Gold Mine). A spiked bore water sample was prepared containing a $7.03 \mu\text{g L}^{-1}$ $[\text{Au}(\text{CN})_2]^-$ spike. Three successive standard additions of $4 \mu\text{g L}^{-1}$ and $8 \mu\text{g L}^{-1}$ of $[\text{Au}(\text{CN})_2]^-$ were added to the unspiked and spiked samples respectively resulting in the standard addition plots shown in Figure 3-4 and Figure 3-5. The resultant plots were linear with correlation coefficients of 0.9982 (unspiked) and 0.9954 (spiked). The $[\text{Au}(\text{CN})_2]^-$ found in the recovery study was 7.7 mg L^{-1} yielding a 110 % recovery on the 7 mg L^{-1} spike.

Table 3-5 Concentrations of $[\text{Au}(\text{CN})_2]^-$ determined with HPLC-ICP-MS.

Slope, linearity and the limit of detection are also reported. $LOD = (s_B + 3.3\sigma_B)/S$, where s_B = signal of the blank, σ_B = standard deviation of the blank and S = slope [171].

Sites	$[[\text{Au}(\text{CN})_2]^-]$ ($\mu\text{g L}^{-1}$)	$[\text{Au}]$ ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	Slope (counts ($\mu\text{g L}^{-1}$) $^{-1}$)	R^2	ICP-MS Total $[\text{Au}]$ ($\mu\text{g L}^{-1}$)
Monitoring bore (Agnew 34)	1.5 ± 0.2	1.2 ± 0.1	0.2	52.32	0.9893	1.15 ± 0.01
Monitoring bore Agnew 27	10.6 ± 0.4	8.4 ± 0.3	0.3	43.55	0.9976	13 ± 2
Monitoring bore (Granites Gold Mine)	9.2 ± 0.4	7.3 ± 0.3	0.1	50.51	0.9989	13.5 ± 0.7
Dewatering pond (Boddington)	0.7 ± 0.1	0.52 ± 0.09	0.1	61.07	0.9916	0.8 ± 0.2

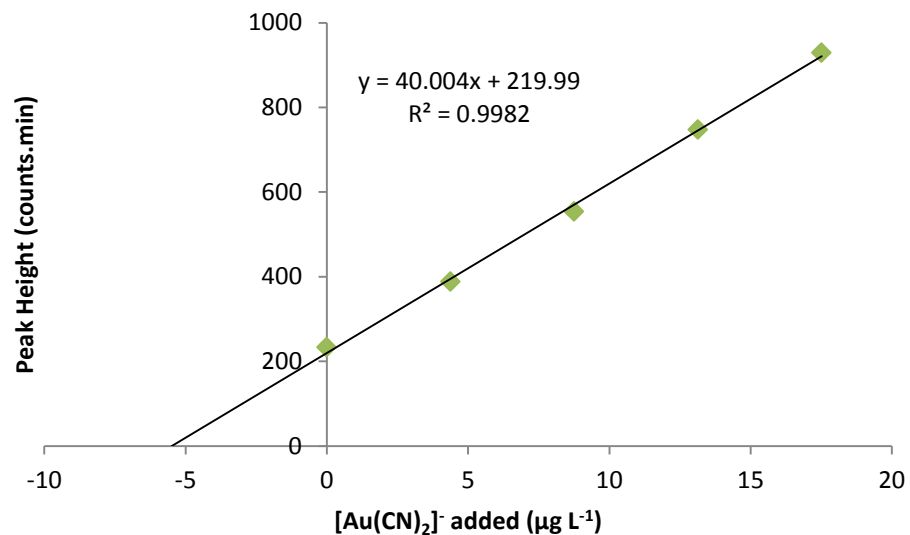


Figure 3-4 Measurement of Au in an unspiked Tanami monitoring bore water.

Calibration plot shows four standard additions of $4 \mu\text{g L}^{-1}$ $[\text{Au}(\text{CN})_2]^-$ to an unspiked water.

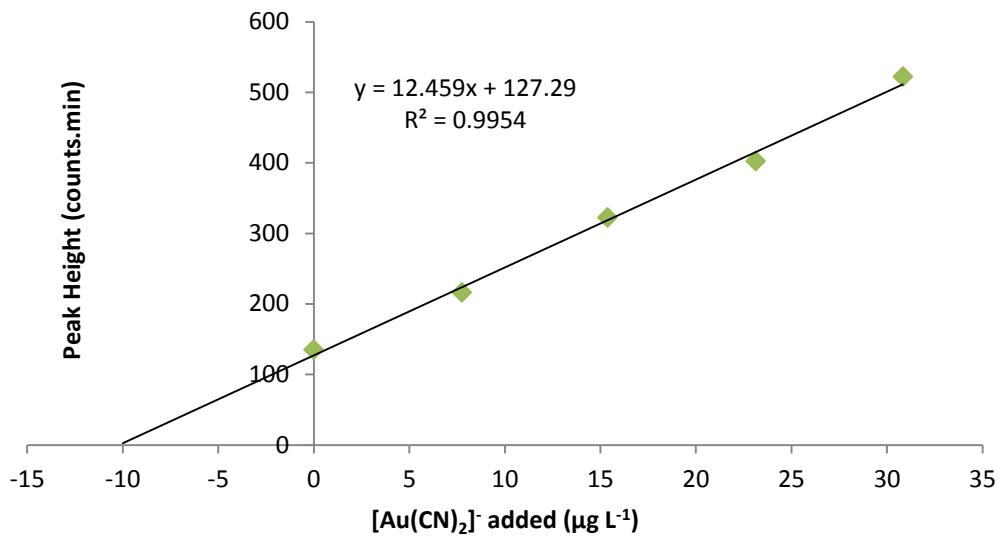


Figure 3-5 Measurement of Au in spiked (7 mg L⁻¹) Tanami monitoring bore water.

Calibration plot shows four standard additions of 8 µg L⁻¹ [Au(CN)₂]⁻ to a spiked water.

Cyanide measurements

The process water and tailings dam samples from Challenger Gold Mine had intense Au(I)-cyanide peaks in the HPLC-ICP-MS analysis Figure 3-4. The intensity of the peaks (~1600 – 2600 counts) were inconsistently high compared to the concentration of total gold detected (~1.3 µg L⁻¹ – 1.9 µg⁻¹). This suggests there might be elevated cyanide levels in the Challenger Gold Mine samples – which are able to remove residual gold bound to the column – resulting in the intense peaks (See Section 2.4.7). To verify this, the water samples were analysed with a cyanide probe (Table 3-6). As expected, CN⁻ ions were only detected in the Challenger samples, therefore, responsible for the intense HPLC-ICP-MS peaks. The ability of cyanide to wash retained gold from the column shows it is necessary to compare the results from HPLC-ICP-MS with the concentrations of total gold from ICP-MS, especially if cyanide is present in the sample. Doing so will allow the elimination of false positives in the detection of Au(I)-cyanide.

Unexpectedly, two samples (from Boddington and Granites Gold Mine) measured positive potential values – when the calibration standards were on a negative log₁₀ scale. So matrix-matching via standard additions was considered, however additions of a cyanide solution to the samples did not reduce the positive potential values. The limitations of the cyanide probe (due to the poor sensitivity (0.1 mg L⁻¹) and possible matrix effects) indicates speciation analysis by HPLC-ICP-MS is preferable to cyanide measurements followed by chemical speciation modelling, for the determination of Au(I)-cyanide in mine waters.

Table 3-6 Cyanide concentrations of mine waters determined by a cyanide probe.

*Note: B.D.L.= samples that are below the specified detection limit of the cyanide probe (0.1 mg L^{-1}) [172]. *Denotes samples that measured a positive potential.*

Sites	[CN ⁻] (mg L ⁻¹)
Monitoring bore (Agnew 27)	B.D.L.
Monitoring bore (Agnew 34)	B.D.L.
Monitoring bore (Granites Gold Mine)	B.D.L.*
Dewatering pond (Boddington)	B.D.L.*
Process water (Challenger Gold Mine)	0.639 ± 0.006
Tailings Dam (Challenger Gold Mine)	3.64 ± 0.01

3.4.3 Application of method to groundwater samples

Speciation chromatograms of the Fifield, British King and Lake Way samples are shown in Figure 3-6. Each sample had a peak at 1.25 minutes, suggesting that a Au(III) complex (such as [Au(OH)₄]) may be present in these groundwaters. However this Au(III) peak is unretained and may comprise of all the unretained components in the sample [173]. Therefore this peak may not be from gold ions but arise from matrix effects.

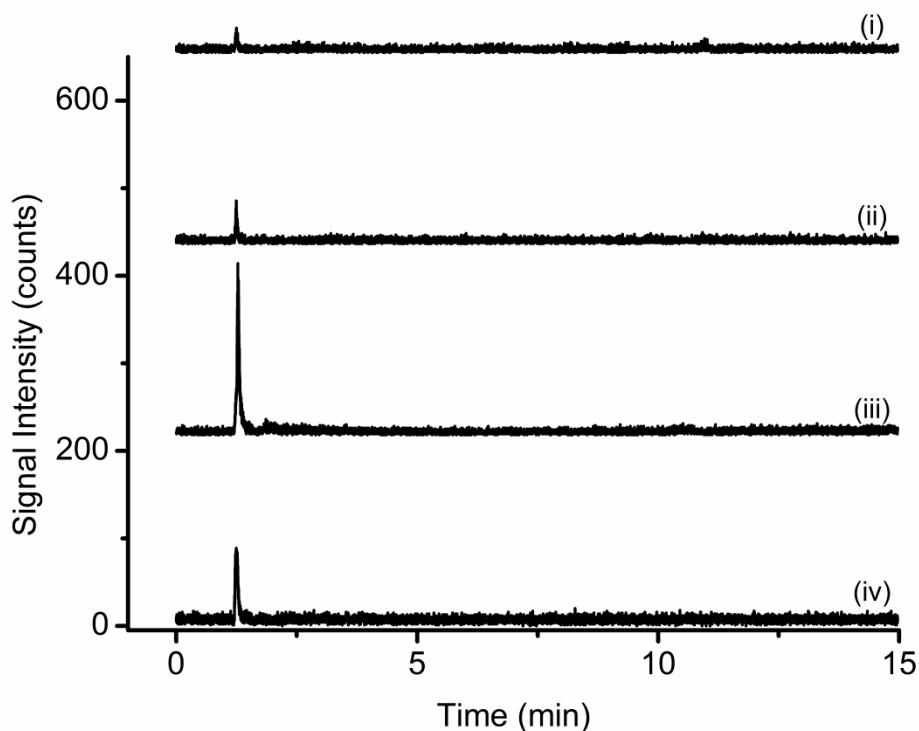


Figure 3-6 Detection of Au(III)-chloride in groundwater samples.

Chromatograms show a possible Au(III)-peak in water samples from: (i) Fifield (Bore 1), (ii) Fifield (Bore 3) (iii) Lake Way and (iv) British King; Mobile phase: 6: 17.5 v/v isopropanol: acetonitrile, 1 mM TBAC, 5 mM NaH₂PO₄/Na₂HPO₄, pH 7.

Therefore it was necessary to shift $[\text{Au}(\text{OH})_4]^-$ peak from the void volume, as the retention times were too similar for spiking to help determine whether the peak was a gold peak or other components in the matrix. In Section 2.4.2 (from the previous chapter), we showed that 50: 50 v/v mixing two ion-pairing agents of different lengths resulted in a retention time that was the average of the two ion-pairing agents; and using 1 mM HDTMAOH in the mobile phase resulted in all the Au-complexes being retained on the column. Consequently a small volume of 1mM HDTMAOH was incorporated into the current mobile phase, (99:1 v/v TBAC: HDTMAOH) in order to increase the retention of the Au(III) complexes.

The retention times of a $96000 \text{ mg L}^{-1} \text{ Cl}^-$ solution and Au(III)-chloride standard in the modified mobile phase are compared in Figure 3-7, (the Cl^- concentration was comparable to the Lake Way (highest Cl^-) see next section). The Cl^- matrix causes a small peak in the void volume. However this matrix effect peak (at 1.3 minutes) was now distinguishable from the $[\text{Au}(\text{OH})_4]^-$ peak (1.64 minutes).

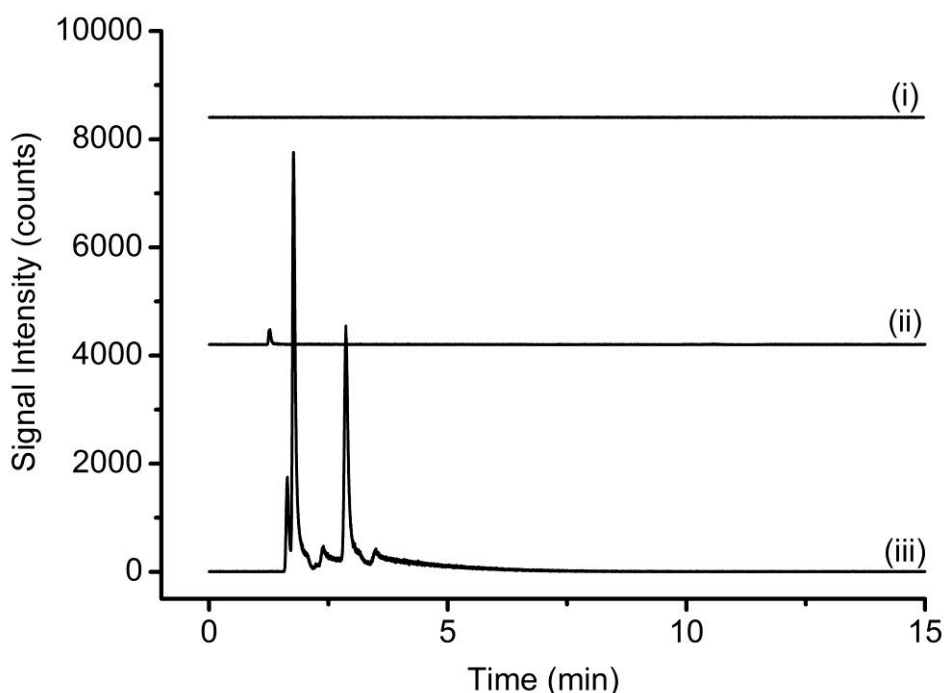


Figure 3-7 Effect of HDTMAOH ion-pairing agent on the retention time of Au-chloride.

Chromatograms of (i) blank, (ii) NaCl (96000 mg L⁻¹) and (iii) 100 mg L⁻¹ of Au-chloride; Mobile phase: 6: 17.5 v/v isopropanol: acetonitrile, 1 mM ion-pairing agent (99:1 v/v TBAC:HDTMAOH), 5 mM NaH₂PO₄/Na₂HPO₄, pH 7.

The groundwater samples of interest were analysed again with the modified mobile phase. The resulting chromatograms in Figure 3-8 show the only samples with gold peaks (shifted peaks) were the Au(III)-chloride standard (one day old) and Lake Way, at 1.64 minutes and 1.9 minutes respectively (the retention times of the other samples remained at 1.27 minutes), The Lake Way chromatogram contains a small peak at 10.2 minutes followed by a noticeable dip (or disturbance) in the signal. Based on results in the previous chapter (Section 2.4.8), the Lake Way sample may also contain a Au(I) complex (which have bound to the cyanide impurities in the mobile phase). The concentration of the Au(III) complexes ($\sim 0.4 \mu\text{g L}^{-1}$) was calculated by the area under the curve.

The Challenger Gold mine samples that exhibited an additional peak around 1.3 minutes (Section 3.4.2) were reanalysed with the modified mobile phase to determine if this peak could be attributed to unretained components from the matrix. The retention time of the peak was unchanged with the new mobile phase, indicating that this peak was from the matrix, not a Au(III) complex (data in Appendix B).

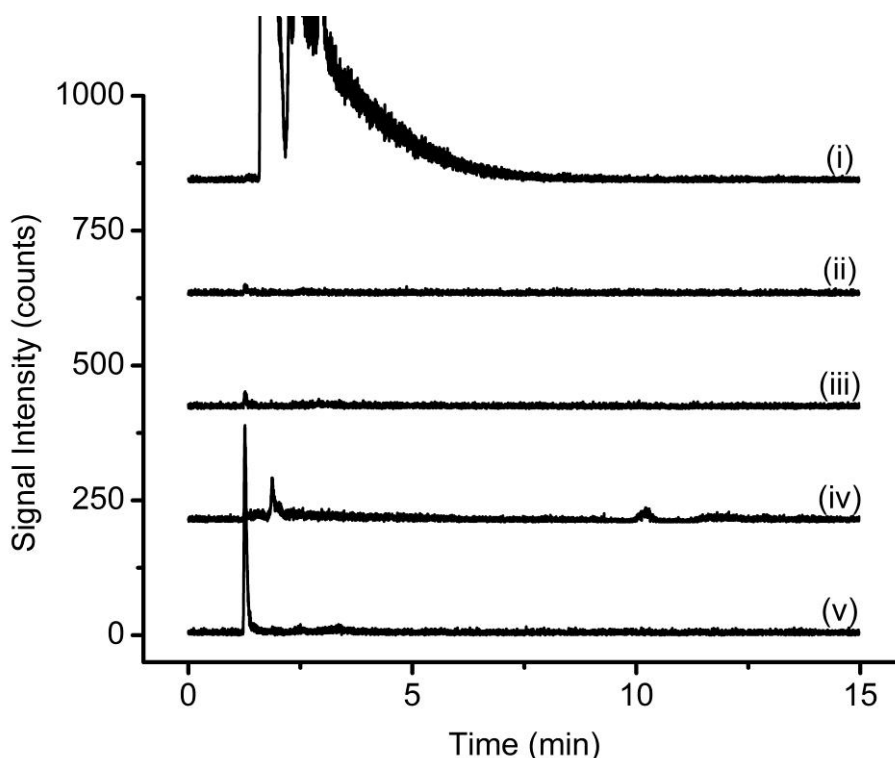


Figure 3-8 Effect of HDTMAOH on peak retention times in various waters.

Chromatograms show (i) 100 mg L^{-1} of Au(III)-chloride, (ii) Fifield (Bore 1), (iii) Fifield Bore 3, (iv) Normandy Salt Lake and (v) British King; Other conditions as Figure 3-7.

3.4.4 Thermodynamic modelling of groundwaters

Chemical analyses of Lake Way and other samples

The previous section describes the possible detection of both Au(I) and Au(III) complexes in the Lake Way water. In order to identify the possible Au-complexes, the chemical composition of the Lake Way water was investigated further. The sample underwent chemical analysis for pH, alkalinity, major anions, carbon, nitrogen and trace elements, etc. The results of the water analysis (displayed in Table 3-7 and Table 3-8) were then used for thermodynamic modelling to determine the possible Au-complexes in the Lake Way sample. The other water samples with the unretained matrix peak (Fifield Bores 1 and 3 and British King) were also analysed for comparison.

All four waters had high concentrations of dissolved salts (such as Cl^- , Na^+ , SO_4^{2-} ions etc.), which may have been responsible for the unretained matrix peaks in their chromatograms (Figure 3-6). The pH of the waters, however, were near-neutral or alkaline ($\sim\text{pH } 7.6 - 8.2$). As discussed earlier (Section 3.1), Au(III) is only stable in acidic and oxidising brines (Figure 3-1), therefore, the detection of Au(III) in the Lake Way water ($\sim\text{pH } 7.6$) was unexpected. Upon comparison of the other trace elements in the waters, it was found that the Lake Way

water contained a high concentration of manganese ($\sim 2.3 \text{ mg L}^{-1}$). According to Howe *et al.* [174], dissolved manganese in natural waters can range from $10 \text{ }\mu\text{g L}^{-1}$ to $>10 \text{ mg L}^{-1}$, but are usually below 0.2 mg L^{-1} . Distribution of species calculations suggest that this level of Mn^{2+} can exist Lake Way waters under mildly reducing conditions ($\log f\text{O}_2 \leq -22$; sulfate stable).

The reduction of Mn(III/IV)-oxide minerals to Mn(II) is often accompanied by the oxidation of metallic ions (such as Co(III), Pb(III), Cr(II/III), As(III), etc.) [175-177]. Additionally, it has been previously suggested by Boyle [1], Emmons [2], Krauskopf [178], and Goldschmidt [179] that manganese is able to oxidise gold. Consequently, the high concentration of Mn^{2+} in the Lake Way water (from the reduction of manganese oxides) may explain the presence of Au(III) in near-neutral waters. Early experiments conducted under acidic conditions have shown that manganese oxides can mobilise gold [180, 181]. To our knowledge, the effect of manganese minerals on the speciation of Au in mild (non-acidic), aqueous conditions are unknown.

Table 3-7 Geochemical analysis of the groundwater from Fifield, Lake Way and British King.

pH, Electrical Conductivity (E.C.), Ammonia-nitrogen (NH₄-N), the sum of Nitrate- and Nitrite- Nitrogen (NO_x-N), Nitrite-nitrogen (NO₂-N) Total nitrogen (TN), total alkalinity, dissolved carbon (DC), inorganic carbon (IC), dissolved organic matter (DOC), and major anions.

Sample	pH	E.C. dS m ⁻¹	NH ₄ -N mg L ⁻¹	NO _x -N mg L ⁻¹	TN mg L ⁻¹	Total Alkalinity meq L ⁻¹	DC mg L ⁻¹	IC mg L ⁻¹	DOC mg L ⁻¹
Detection limits	-	0.01	0.005	0.005	0.1	0.1	0.5	0.1	0.5
Fifield Bore 1	7.97	21.69	0.012	0.190	0.2	10.1	120.3	104.2	16.1
Fifield Bore 3	8.15	17.37	0.410	0.050	0.5	7.8	109.3	94.4	14.9
British King	7.85	26.20	0.177	<0.005	0.7	4.8	64.4	52.4	12.0
Lake Way	7.64	135.3	4.747	0.415	2.4	0.6	20.5	7.5	13.0

Sample	[†] Cl ⁻ mg L ⁻¹	[†] Br ⁻ mg L ⁻¹	[†] NO ₃ ⁻ mg L ⁻¹	[†] SO ₄ ⁼ mg L ⁻¹	[*] Ca mg L ⁻¹	[*] K mg L ⁻¹	[*] Mg mg L ⁻¹	[*] Na mg L ⁻¹	[*] S mg L ⁻¹	[*] Si mg L ⁻¹	[*] Sr mg L ⁻¹
Detection limits	0.05	0.05	0.05	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.05
Fifield Bore 1	7900	28	2.4	4300	401	10.8	1090	4210	1340	4.0	7.77
Fifield Bore 3	4700	14	3.2	4400	208	<1	341	3930	1360	9.5	3.40
British King	7500	13	<2	4700	157	59.5	236	5810	1430	<1.25	2.75
Lake Way	96000	53	<20	41000	327	5680	8130	49700	8560	<5.0	7.08

Notes: NO₂-N < 0.005 mg L⁻¹. (†) Elements analyzed by ion chromatography; F⁻ <2 mg L⁻¹. (*) Elements analysed by ICP-OES; Al, As, Cd, Co, Cu, Ni, Pb, Se, Zn < 0.5 mg L⁻¹; B, Fe, P, Sb < 1 mg L⁻¹.

Table 3-8 ICP-MS analysis of the groundwater from Fifield, Lake Way and British King.

Sample:	Mn	Cr	Fe	Co	Ni	Cu	Ga	Ge	As	Se	Nb	Cd	Te	Sm	W	Th	U
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Detection limits	0.2	0.2	0.2	0.2	0.8	0.2	0.04	0.2	0.5	1	2	0.6	1	0.2	0.1	0.2	0.2
Fifield Bore 1	390	0.63	<0.2	<0.2	1.2	<0.2	2.9	0.63	0.77	9.2	5.4	2	2.9	0.25	26	0.24	2.3
Fifield Bore 3	75	<0.2	<0.2	2.5	3.3	2.1	0.81	<0.2	11	<1	2.7	0.9	4.3	<0.2	15	0.22	<0.2
British King	74	32	480	1.36	6	<6	<0.4	<6	<10	3	1.2	0.2	1.6	0.08	1.2	<0.2	0.62
Lake Way	2300	<10	600	8.4	5	20	<1	<20	<30	12	4	1.4	<2	0.4	2	<0.5	8.05

Notes: The following elements were analyzed but found to be below detection limit: Sc, V, Y, Pd, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Re, Pt, Pb < 0.2 µg L⁻¹, Zn < 1 µg L⁻¹; Ag < 0.1 µg L⁻¹.

Predicted modelling of Au species in Lake Way

Figure 3-9 (A) is a plot of possible gold species in Lake Way at sliding oxygen fugacity. The plot shows at the conditions described in Table 3-7 and Table 3-8, the presence of Au(III)-complexes is thermodynamically unexpected (as discussed in Section 3.1). At oxygen fugacities (fO_2) above 10^{-12} atm, Au(I) complexes: $[AuCl(OH)]^-$, $[AuCl_2]^-$, $[Au(OH)_2]^-$, $[AuBr(OH)]^-$, $AuCl(aq)$, and $[AuBr_2]^-$ are stable (gold begins to precipitate below $fO_2 = 10^{-12}$ atm). The current model predicts that at equilibrium Au(III)-complexes should not be the major complex, contradicting the HPLC-ICP-MS analysis (Section 0). Even at over-oxygenated conditions, $fO_2 = 1$ atm the Au(III)-complexes never reach equilibrium. The current thermodynamic values in aqueous gold modelling are from theoretical calculations or measurement of model solutions [71, 72, 84, 85], as previously, there was no direct method of determining the speciation of gold in natural waters. For the first time the speciation of aqueous gold in natural waters can be directly measured and it is likely that some old thermodynamic models will need to be reconsidered.

In an effort to identify the Au(III) species in Lake Way, only Au(III) ions were modelled in the presence of Br^- and Cl^- ions. The resultant log activity-pH speciation diagram in Figure 3-9 (B) gives the speciation of gold if the system was constrained to Au(III)-complexes. At pH 7.9 and the calculated Br^- and Cl^- activities the major gold species are predicted to be $[Au(OH)_2Cl_2]^-$, $[Au(OH)_3Br]^-$ and $[Au(OH)_3Cl]^-$ (indicated by the yellow star). The broad peak in the Lake Way chromatogram (Figure 3-8 (iv)) is probably made up of these species.

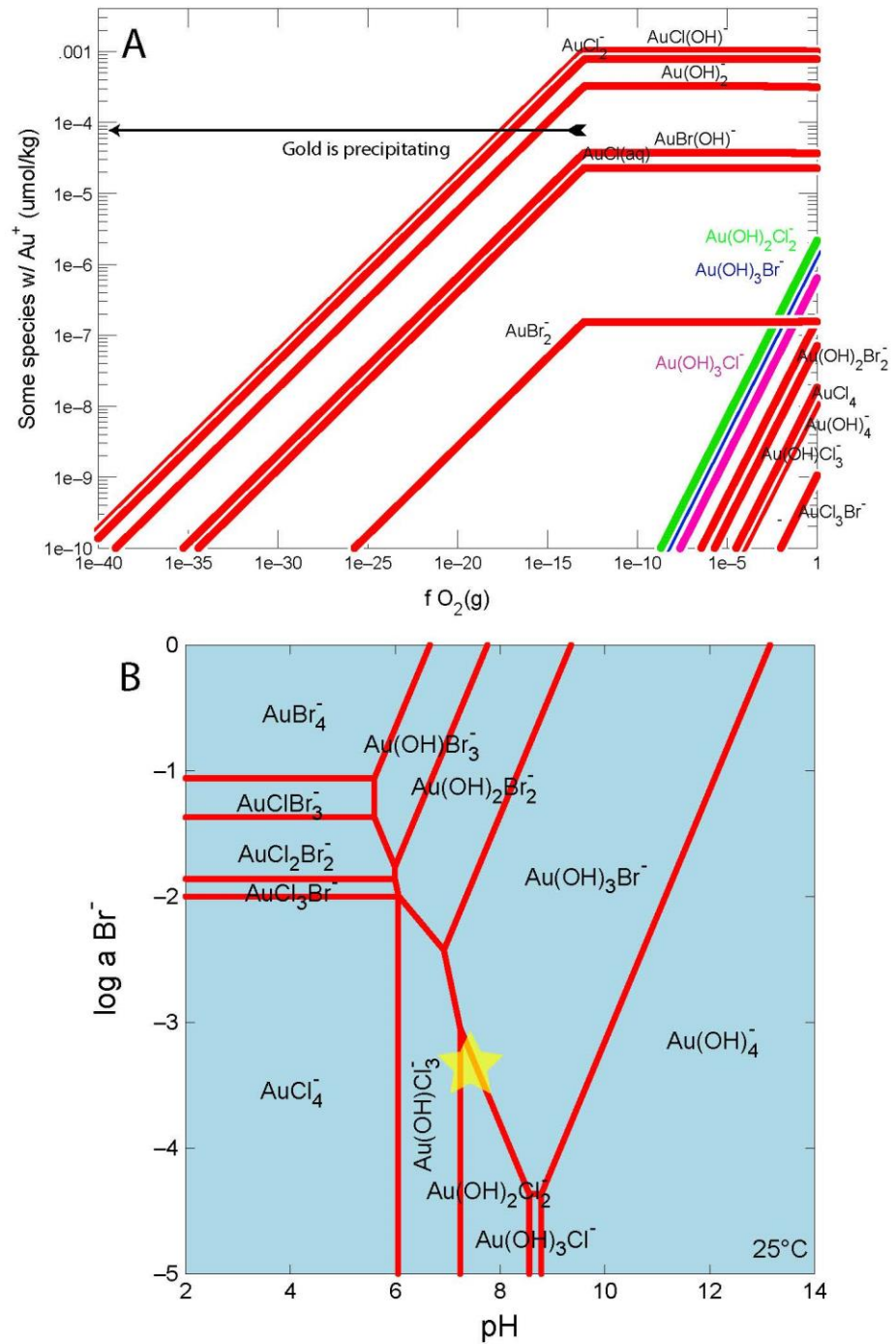


Figure 3-9 Thermodynamically predicted gold species for Lake Way.

Plots show (A) reaction path of Au species at sliding fugacity (the arrow shows where gold precipitates); and (B) likely Au(III)-species at sliding pH when Au(I) species are suppressed (the yellow star marks the pH and log a[Br⁻] of the Lake Way sample).

3.4.5 Implications on gold mobility

Mine waters

Cyanide is the major lixiviant used for the recovery of gold from complex ores [182]. Therefore the detection of Au(I)-cyanide in the Boddington dewatering pond (water that has been removed from mine waste material) and the Challenger Gold Mine process water and tailings was expected. However, trace amounts of Au(I)-cyanide were also detected in environmental monitoring bores located in both the Granites and Agnew Gold Mines sites. Although further studies are required to follow the formation and distribution of Au(I)-cyanide, the proximity of these monitoring bores to the tailings dams and other mining processes suggests that the Au(I)-cyanide is due to anthropogenic cyanide (from leaching processes and not cyanide producing plants or microorganisms). Our findings confirm Leybourne *et al.*'s [94] transport model of gold in stream waters draining an old gossan tailings pile. Leybourne *et al.* [94] attributed the elevated gold levels (up to $19 \mu\text{g L}^{-1}$) to mobilised Au(I)-cyanide, $[\text{Au}(\text{CN})_2]^-$, from the cyanide leaching used to process the gossan for gold. However Leybourne *et al.*'s [94] assessment was through chemical speciation modelling, while we were able to directly determine the speciation of gold to be Au(I)-cyanide.

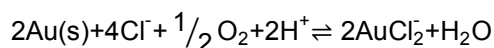
Previous studies of tailings dams have predominantly focussed on the mobility of arsenic, mercury and other metal contaminants (i.e. Cu, Zn, Pb, Co and Ni) [183-186], however, studies on the mobilisation/fate of gold in tailings may provide information for (and improve) reclamation processes of existing tailings dams for the recovery of gold. These studies are necessary since the use of cyanide leaching does not guarantee the perpetual existence of gold in the Au(I)-cyanide form (Leybourne *et al.* [94] attributed the decreasing gold concentrations, further downstream from the gossan tailings pile, to Au(I)-cyanide reduced to nanoparticles). Gold recovery methods include the dissolution and precipitation of gold, flotation or phytoextraction (uptake by plants) – processes which are dependent on the form of gold [187-189]. Therefore effective recovery is dependent on understanding the form and distribution of gold, an understanding that may be improved with future analysis of tailings dams and the surrounding waters with HPLC-ICP-MS analysis.

Although free cyanide was not detected in these monitoring bores and the trace amounts of Au(I)-cyanide found are below the weak acid dissociable cyanide concentrations deemed safe for wildlife (below 50 mg L^{-1}) [169], it is important to note this assessment does not include any other cyanide complexes that may be present in these waters.

Groundwaters

Gold was also detected in water samples from Sunlight Gold Mine, Oberon, British King, Darlot Batterie, Plutonic West 2, Wildara, Fifield Bores and Lake Way with ICP-MS. These samples are in known auriferous zones and support findings that dissolved gold concentrations are higher in auriferous zone and therefore able to be used as a pathfinder for gold mineralisation [149, 157]. Speciation analysis with HPLC-ICP-MS, however, only showed gold in the Lake Way sample (the peaks detected in the British King and Fifield samples are attributed to matrix interferences). We think this is due to the gradual removal of the gold from solution due to adsorbance of the gold to the walls of the storage bottles over time (Section 4.4.1). This would account for the discrepancy between the HPLC-ICP-MS and ICP-MS results, as HPLC-ICP-MS was carried out months after the initial ICP-MS analysis. The groundwater samples may be more susceptible to this adsorbance effect than the mine waters due to the presence of cyanide in the mine water matrix. Leybourne *et al.* [94] also found very little gold was removed from solution when the gold was complexed to a strong ligand such as cyanide. This may explain why Au(I)-thiosulfate, $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$, was not detected in any of the samples, even though waters were sampled from mineralised zones, where $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ is considered to be an important form of mobilised gold [72, 149].

HPLC-ICP-MS analysis showed that Au(I) and Au(III) complexes were possibly present in the Lake Way water. The Lake Way sample is very saline, and has a near-neutral pH (~pH 7.6). According to current modelling, Au(III) complexes are not thermodynamically stable at any oxygen fugacity (Figure 3-9), and could only be Au(I) complexes (a mixture of $[\text{AuCl}(\text{OH})]^-$, $[\text{AuCl}_2]^-$, $[\text{Au}(\text{OH})_2]^-$, $[\text{AuBr}(\text{OH})]^-$, $\text{AuCl}(\text{aq})$, and $[\text{AuBr}_2]^-$ complexes). Similarly, models done by Gray and Pirlo [93, 103] on saline waters (in Tunkillia and the Yilgarn Craton, Australia), predicted the speciation of gold to be gold(I)-halides (i.e. AuCl_2^- , AuI_2^-). According to the Gray and Pirlo [93], the dominant mechanism for the mobilisation of gold in Cl^- rich waters is:



Although equilibrium thermodynamics predict Au(I)-chloro-hydroxyl complexes to be dominant, the stability constants used in the model have been derived from experiments conducted under hydrothermal conditions (>100 °C), where such complexes are most stable and have not been measured at surface temperatures [82, 190]. Up until now, there has been no direct method for the speciation of gold and the Au(III) redox state has not been considered by these models.

Although Gray [103] found no apparent correlation between dissolved manganese and gold, a comparison of the chemical composition of the Lake Way sample with the other saline samples (Fifield bores and British King), suggests there is a correlation between the dissolved manganese (~2.3 mg L⁻¹) and the Au(III) redox state in the Lake Way sample. It

has been reported by a number of authors that manganese may be able to mobilise gold in the environment [1, 2, 178, 179], however, this has only been demonstrated by the dissolution of gold with manganese oxides under acidic conditions, where the speciation gold was not directly measured [180, 181]. Therefore, further work investigating the effect of manganese on the speciation of gold under less extreme conditions is required. To our knowledge, the effect of manganese minerals on the speciation of Au under mild (non-acidic) conditions is unknown.

3.5 Conclusions

Of the sixty two water samples collected from around Australia, trace amounts of $[\text{Au}(\text{CN})_2]^-$ was found in the monitoring bores located within Agnew, Boddington, and the Granites Gold Mine, which may be due to leaching from mining processes. Au(I) and Au(III) complexes were detected in the Lake Way water, however, only Au(I) complexes were predicted by chemical speciation modelling. Chemical analysis of several saline groundwaters suggests Au(III) may be correlated with manganese. Therefore, current thermodynamic models (which only predict Au(I)-complexes to be stable in natural waters), and may need to be adjusted in regards to the effect of manganese on gold. This is explored further in the next chapter, where the effect on various manganese compounds on the redox of Au(0) and Au(I) are monitored by HPLC-ICP-MS.