

## Analysis of Gold(I/III)-Complexes by HPLC-ICP-MS Demonstrates Gold(III) Stability in Surface Waters

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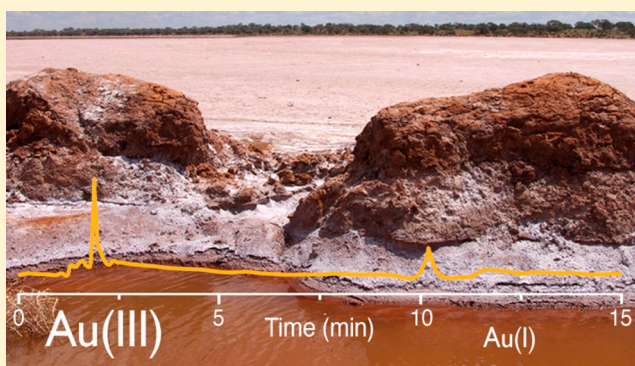
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**S** Supporting Information

**ABSTRACT:** Understanding the form in which gold is transported in surface- and groundwaters underpins our understanding of gold dispersion and (bio)geochemical cycling. Yet, to date, there are no direct techniques capable of identifying the oxidation state and complexation of gold in natural waters. We present a reversed phase ion-pairing HPLC-ICP-MS method for the separation and determination of aqueous gold(III)–chloro-hydroxyl, gold(III)–bromo-hydroxyl, gold(I)–thiosulfate, and gold(I)–cyanide complexes. Detection limits for the gold species range from 0.05 to 0.30  $\mu\text{g L}^{-1}$ . The  $[\text{Au}(\text{CN})_2]^-$  gold cyanide complex was detected in five of six waters from tailings and adjacent monitoring bores of working gold mines. Contrary to thermodynamic predictions, evidence was obtained for the existence of Au(III)-complexes in circumneutral, hypersaline waters of a natural lake overlying a gold deposit in Western Australia. This first direct evidence for the existence and stability of Au(III)-complexes in natural surface waters suggests that Au(III)-complexes may be important for the transport and biogeochemical cycling of gold in surface environments. Overall, these results show that near- $\mu\text{g L}^{-1}$  enrichments of Au in environmental waters result from metastable ligands (e.g.,  $\text{CN}^-$ ) as well as kinetically controlled redox processes leading to the stability of highly soluble Au(III)-complexes.



## INTRODUCTION

The mobility of gold in surface environments is substantiated by a large body of evidence based on determining the products of (bio)geochemical gold redistribution. Current consensus assumes that the mobilization and transport of gold in aqueous systems occurs via (in)organic gold complexes and/or nanoparticles, whose formation is mediated by a number of biogenic and abiogenic processes, in particular affecting the formation of metastable ligands such as cyanide and thiosulfate.<sup>1</sup> Direct evidence for the formation of these complexes is absent as the low levels of gold found in natural waters ( $\leq 1 \mu\text{g L}^{-1}$  for groundwaters<sup>2–4</sup>) have made direct speciation analysis impossible to date. Existing predictions are based on extrapolations of experimental data generated at elevated concentrations (typically  $\text{mg L}^{-1}$ ), thermodynamic calculations, and environmental abundances of suitable ligands.<sup>5–7</sup> In general, these predictions agree that (i) in environments containing little organic carbon the dominant gold complex is  $[\text{Au}(\text{I})\text{OH}(\text{H}_2\text{O})]^0$ ; (ii) Au(I)– and potentially Au(III)–chloride (and their corresponding mixed chloride-hydroxide complexes) occur in highly acidic oxidizing waters containing high concentrations of chloride; (iii) Au(I)–

thiosulfate complexes are formed in the presence of gold-bearing sulfide minerals; and (iv) Au(I)–cyanide exists in areas with trace amounts of cyanide from mine processing, or cyanide-releasing plants and microorganisms.<sup>6,8</sup> However, without directly measured environmental data our understanding of gold speciation in natural waters remains highly speculative.

Direct speciation analysis of low levels of aqueous gold will provide information about the mechanisms of gold mobilization in the environment, and can be used to guide the interpretation of regional hydrogeochemical exploration data sets. Similarly, direct measurement of gold speciation is essential for environmental monitoring and (bio)remediation of tailings and waters from gold mining sites.<sup>9</sup> Additionally, gold speciation can also be used to guide the choice and concentration of lixiviant used in gold leaching and for the

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targeted design of recovery strategies for low level aqueous gold.<sup>10,11</sup>

High performance liquid chromatography–inductively coupled plasma–mass spectrometry (HPLC-ICP-MS) is capable of determining the speciation of trace elements, particularly As, Se, and Sb.<sup>12,13</sup> HPLC allows the separation of metal-, organometallic-, and protein complexes,<sup>14–16</sup> whereas ICP-MS offers trace element detection limits in the low to sub ng L<sup>-1</sup> range. Thus, it is ideally suited for the speciation of trace levels of gold in aqueous solution. A small number of studies have identified aqueous gold species using HPLC-ICP-MS methodologies. These used ion-exchange, size-exclusion and reversed phase chromatographic methods and achieved detection at levels that ranged from sub µg L<sup>-1</sup> to mg L<sup>-1</sup>.<sup>17–20</sup> None of these studies have assessed natural waters or waters associated with mining operations. We report a HPLC-ICP-MS method for the detection of Au(I)–thiosulfate, Au(I)–cyanide, and Au(II)I-chloro-hydroxyl and Au(III)–bromo-hydroxyl complexes at µg L<sup>-1</sup> levels in surface- and groundwater samples. The method was used to monitor gold hydrolysis and ligand exchange in standard solutions. It was then applied to measure the speciation of gold in environmental samples, namely in tailings waters, waters from monitoring bores close to mine sites using cyanide leaching, and in a surface water from an alkaline hypersaline lake overlying a buried gold deposit.

## EXPERIMENTAL SECTION

**Reagents and Standards.** All chemicals were of analytical grade and all solvents HPLC grade, unless otherwise stated. Ultrahigh purity water (Millipore, Australia) was used throughout. Sodium tetrabromoaurate, sodium gold(I) thiosulfate, and potassium gold(I) cyanide were purchased from Strem Chemicals Inc. (Newburyport, MA). Stock solutions (100 mg L<sup>-1</sup> total Au) of the gold complexes were prepared gravimetrically in plastic by dissolving the appropriate amount in water and stored in the dark to prevent the photolytic precipitation of gold.<sup>21</sup> Gold(I) cyanide stock solutions were prepared in pH 12 (0.01 M) NaOH solution to prevent the generation of HCN gas. Stock solutions of gold(III) chloride (100 mg L<sup>-1</sup> Au) were prepared by appropriate dilution of a 1000 mg L<sup>-1</sup> gold ICP-MS Standard (in 2% HCl, Choice Analytical, Australia) with water. Stock solutions were diluted to 100 µg L<sup>-1</sup> total Au with the mobile phase immediately prior use. The gold tune solution (1.0 µg L<sup>-1</sup> Au) was prepared by dilution of a 1000 mg L<sup>-1</sup> Au(III)–chloride ICP-MS Standard (in 2% HCl, Choice Analytical, Australia) with the mobile phase. All cationic ion-pairing agents were obtained from Sigma-Aldrich (Castle Hill, Australia). The mobile phase composition was 6:17.5:76.5 v/v/v isopropanol: acetonitrile: water, 1 mM tetrabutylammonium chloride (TBA-Cl), 5 mM NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub> (adjusted to pH 7.0 with H<sub>3</sub>PO<sub>4</sub>).

**Instrumentation.** Chromatographic separations were achieved using an Agilent 1200 Series HPLC coupled with an Agilent 7500cx ICP-MS. The HPLC-ICP-MS operating conditions and the operation procedure are detailed in the Supporting Information (SI) (Table S1).

**Hydrolysis and Exchange Experiments.** Freshly prepared standards of Au(III)–chloride, Au(III)–bromide, Au(I)–thiosulfate, and Au(I)–cyanide ([Au] = 100 µg L<sup>-1</sup>) were monitored for hydrolysis over 480 min. Ligand exchange was observed in solutions comprising of a mix of the four gold standards (20 µg L<sup>-1</sup> each).

**Natural Water Samples.** Water samples were obtained from a number of sites in Australia (Table 1). The sampling

**Table 1. Locations of the Waters Used in this Study**

sample description	code	location
monitoring bores (downstream of tailing ponds)	M1	Agnew Gold Mine, Western Australia (WA), Australia (Bore 27) 28° 01' 11" S, 120° 29' 48" E
	M2	Agnew Gold Mine, WA, Australia (Bore 34) 28° 01' 13" S 120° 29' 34" E
	M3	Granites Gold Mine, Northern Territory, Australia, 20° 32' 35" S, 130° 19' 33" E
dewatering pond (in an open cut mine)	D	Boddington, WA, Australia, 32° 45' 08" S, 116° 21' 19" E
capped mine tailings	T	Hillgrove Mine, New South Wales, Australia, 30° 34' 35" S, 151° 54' 35" E
drainage channel in salt lake	L	Lake Way, WA, Australia, 26° 45' 32" S, 120° 16' 56" E

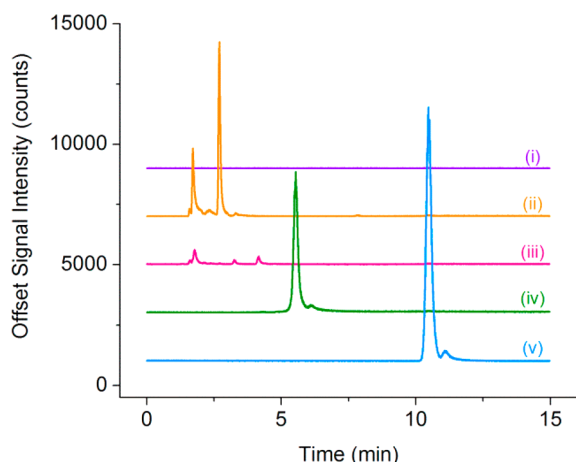
procedure follows the method detailed in Brugger et al.<sup>22</sup> All samples were brought to room temperature and syringe-filtered (PDVF, 0.45 µm) before analysis. Elemental analyses were conducted by the Analytical Chemistry Unit, CSIRO Land and Water, Adelaide (see SI). [Au(CN)<sub>2</sub>]<sup>-</sup> 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. For the spike-and-recovery analysis a bore water sample (Granites Gold Mine) was analyzed both in the absence and presence of a spike (7 µg L<sup>-1</sup> [Au(CN)<sub>2</sub>]<sup>-</sup>). The level of gold in the unspiked sample was determined using four successive standard additions of 4 µg L<sup>-1</sup> of [Au(CN)<sub>2</sub>]<sup>-</sup>. The level of gold in the spiked sample was determined using four successive standard additions of 8 µg L<sup>-1</sup> of [Au(CN)<sub>2</sub>]<sup>-</sup>.

**Thermodynamic Equilibrium Modeling.** Geochemist's Workbench software (Aqueous Solutions LLC, Huntington, WV)<sup>23</sup> 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 gold complexes from Usher et al.<sup>7</sup>

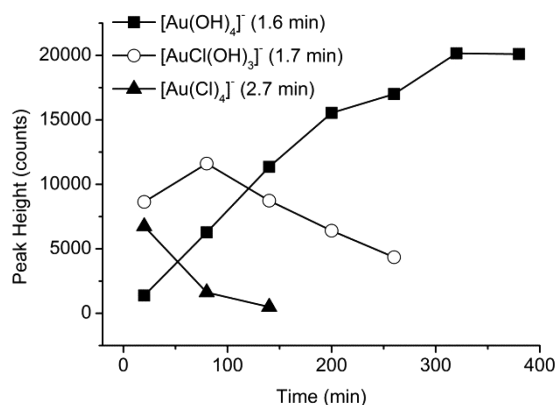
## RESULTS AND DISCUSSION

**HPLC Method Development.** Method development was undertaken by evaluating individual solutions (100 µg L<sup>-1</sup>) made from the Au(III)–bromide, Au(III)–chloride, Au(I)–thiosulfate, and Au(I)–cyanide standards. This was undertaken because gold complexes can be labile in solution.<sup>7,24</sup> Hence, individual standards were used to avoid interactions among the different species.

Initial HPLC conditions were based on those of Zhao et al.<sup>20</sup> Method development is described in the SI. The final separation conditions were 6:17.5:76.5 v/v/v isopropanol:acetonitrile:water, 1 mM tetrabutylammonium chloride (TBA-Cl), 5 mM NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub> (adjusted to pH 7.0 with H<sub>3</sub>PO<sub>4</sub>). The resulting separation is shown in Figure 1. It must be noted that although 1 mM Cl<sup>-</sup> ion from the TBA-Cl may affect the speciation of the Au(III)–halide complexes in samples with low chloride concentrations, typical samples of interest contain an excess of chloride. According to Gray,<sup>2</sup> salt solutions with soluble gold (Au > ~0.2 mg L<sup>-1</sup>) contain at least 10 mM Cl<sup>-</sup> (at pH 0–3) to 100 mM Cl<sup>-</sup> (pH 0–5.5). Moreover, typical Australian brines contain ~2400 to 5300 mM of chloride.<sup>25</sup> At these high concentrations of chloride, the speciation of gold will be unaffected by the use of TBA-Cl. Additionally, the use of



**Figure 1.** Developed HPLC-ICP-MS method; Chromatograms of gold standards showing (i) Blank, (ii) Au(III)–chloro-hydroxyl complexes, (iii) Au(III)–bromo-hydroxyl complexes, (iv) Au(I)–thiosulfate, and (v) Au(I)–cyanide. Mobile phase: 1 mM TBAC, 5 mM NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub>, pH 7 (adjusted with H<sub>3</sub>PO<sub>4</sub>), and 6:17.5:76.5 v/v/v isopropanol:acetonitrile:water.



**Figure 2.** Effect of dilution and aging time on the speciation of the Au(III)–chloride standard (20 mg L<sup>−1</sup>, in water). [AuCl<sub>2</sub>(OH)<sub>2</sub>]<sup>−</sup> and [AuCl<sub>3</sub>OH]<sup>−</sup> (2.2 and 2.3 min, respectively) were near detection limit and are not plotted here.

corresponding to each of the five possible [AuCl<sub>(4−n)</sub>(OH)<sub>n</sub>]<sup>−</sup> 214 complexes; the largest eluted at 1.7 min (likely to be the 215 [AuCl(OH)<sub>3</sub>]<sup>−</sup> complex). As can be seen in Figure 2, the 216 [Au(OH)<sub>4</sub>]<sup>−</sup> peak continues to increase in intensity over time 217 as the equilibrium between the Au(III)–chloride complexes 218 and water shifts toward the formation of the hydroxide 219 complex. This result is consistent with that of Lee and 220 Gavriilidis<sup>29</sup> who suggested that the initial dominant complexes 221 were AuCl<sub>2</sub>(H<sub>2</sub>O)OH, [AuCl<sub>2</sub>(OH)<sub>2</sub>]<sup>−</sup>, [AuCl(OH)<sub>3</sub>]<sup>−</sup>, and 222 [Au(OH)<sub>4</sub>]<sup>−</sup>, respectively, while the dominant complexes at 223 720 min were [AuCl<sub>2</sub>(OH)<sub>2</sub>]<sup>−</sup>, [AuCl(OH)<sub>3</sub>]<sup>−</sup>, and [Au- 224 (OH)<sub>4</sub>]<sup>−</sup>.<sup>29</sup> Although Lee and Gavriilidis<sup>29</sup> prepared their 225 standards differently (higher gold concentration, 2.5 × 10<sup>−3</sup> M 226 HAuCl<sub>4</sub>, and pH adjusted with 0.1 M Na<sub>2</sub>CO<sub>3</sub>), they also 227 observed an equilibrium shift toward the formation of the 228 hydroxide complexes at pH 5–11. Similarly to their study, the 229 equilibrium shift toward [Au(OH)<sub>4</sub>]<sup>−</sup> dominance occurs over 230 hours. The Au(III)–bromide standard also underwent similar 231 changes in speciation toward the formation of the hydroxide 232 complexes (SI, Figure S4). These results indicate that 233 groundwater samples should be analyzed without predilution 234 or concentration if possible. Where samples are manipulated, 235 they should be left overnight to allow the speciation of gold to 236 equilibrate. 237

Ligand exchange upon mixing different Au(III) and Au(I) 238 complexes was observed for a series of mixed gold standards 239 over time (SI, Figure S5). Importantly, the Au(III)–halide 240 peaks were broadened and coelution was observed. This is 241 likely to be due to the 18 possible mixed complexes 242 [AuX<sub>(4−n)</sub>(OH)<sub>n</sub>]<sup>−</sup> (where X = Cl, Br or a mixture of both, 243 and n = 0–4) that could have formed upon mixing of Au(III)– 244 chloride and Au(III)–bromide in water. Consequently, 245 individual standards must be used for quantification to avoid 246 interactions that may occur between the different species. 247 Therefore, an initial screening run to determine likely 248 speciation followed by matrix matching using standard 249 additions was used for quantifying gold species. 250

**Analytical Figures of Merit.** As discussed above, the 251 quantification of gold cannot be achieved with a mixed gold 252 standard. Instead, the samples must first be screened to identify 253 the gold species. Determination of the species can then be 254 performed using calibration curves prepared from the 255 appropriate individual standard solutions. Calibration curves 256 of the individual standards were linear in the region 0.25 μg L<sup>−1</sup> 257 12

174 acetonitrile introduces a possible source of cyanide contami-  
175 nation from the mobile phase,<sup>26</sup> however, this is only important  
176 for samples containing low levels of gold (see Analytical Figures  
177 of Merit).

178 **Effect of Hydrolysis and Ligand Exchange on Sample**  
179 **Preparation Regime.** It is well documented that gold  
180 complexes are labile in solution, with the overall speciation  
181 being affected by the solution pH and ionic composition of the  
182 aqueous environment. For example, Au(III)–chloride and  
183 Au(III)–bromide can be readily hydrolyzed to form mixed  
184 halide complexes.<sup>7</sup> Spectroscopic studies monitoring the  
185 hydrolysis of Au(III)–chloride,<sup>24,27,28</sup> and the exchange of  
186 chloride and bromide ligands in Au(III)–complexes<sup>7</sup> have  
187 previously been undertaken at gold concentrations (~20 to  
188 2000 mg L<sup>−1</sup>), which are much higher than those detected in  
189 surface- and groundwaters.<sup>7,24,27,28</sup> In light of this, and the  
190 effect this could have on sample and standard preparation, we  
191 tested a series of standards at lower concentrations to inform  
192 our sample and standard preparation procedures.

193 Hydrolysis of freshly prepared standards of Au(III)–chloride,  
194 Au(III)–bromide, Au(I)–thiosulfate, and Au(I)–cyanide  
195 (diluted to an environmentally relevant concentration of 100  
196 μg L<sup>−1</sup>) was monitored every 60 min for 480 min, starting at t =  
197 20 min. The resulting chromatograms and peak height plots  
198 (SI, Figures S1 and S2) show that the speciation of Au(I)–  
199 thiosulfate and Au(I)–cyanide remain unchanged for the  
200 duration of the experiment. However, a substantial change in  
201 speciation was observed for the Au(III)–chloride standard  
202 (Figure 2, chromatograms shown in SI, Figure S3), where over  
203 time the number of Au(III)–chloride peaks reduced from five  
204 peaks (t = 20 min) to two peaks (t = 480 min). This can be  
205 explained by the dilution of the 1000 mg L<sup>−1</sup> Au(III)–chloride  
206 stock solution (2% HCl). The acidity (pH 0) and chloride  
207 concentration (5.5 × 10<sup>−1</sup> M) stabilizes the [AuCl<sub>4</sub>]<sup>−</sup> complex.  
208 Upon dilution with water, the concentration of the chloride  
209 decreases to 5.5 × 10<sup>−6</sup> M and the pH increases to ~2. The  
210 labile chloride ligand is subsequently hydrolyzed, resulting in  
211 the formation of the (mixed) hydroxide complexes  
212 [AuCl<sub>(4−n)</sub>(OH)<sub>n</sub>]<sup>−</sup>, where n = 0–4. The rate of change in  
213 speciation is quite rapid: at t = 20 min five peaks were observed,



to 50  $\mu\text{g L}^{-1}$ . As shown in Table 2, the detection limits for the gold complexes are in the sub ng  $\text{L}^{-1}$  level. The LOD and LOQ

Table 2. Analytical Figures of Merit<sup>a</sup>

	slope (counts min <sup>-1</sup> )	R <sup>2</sup> value	LOD ( $\mu\text{g L}^{-1}$ )	LOQ ( $\mu\text{g L}^{-1}$ )
total Au(III)–chloro-hydroxyl complexes	102.9 ± 0.7	0.9997	0.05	0.16
total Au(III)–bromo-hydroxyl complexes	48.0 ± 0.2	0.9999	0.10	0.34
Au(I)–thiosulfate	16.9 ± 0.4	0.9980	0.30	1.0
Au(I)–cyanide	40.1 ± 0.2	0.9999	0.13	0.42

<sup>a</sup>Limit of detection (LOD) =  $3\sigma_B/S$ , where  $\sigma_B$  = standard deviation of the blank and  $S$  = slope; limit of quantification (LOQ) =  $10\sigma_B/S$ .<sup>30</sup> Standards were allowed to equilibrate overnight.

values are for the Au(I)–thiosulfate complex (0.58  $\mu\text{g L}^{-1}$  and 1.4  $\mu\text{g L}^{-1}$  respectively), where in standards 1  $\mu\text{g L}^{-1}$  and below, a small Au(I)–cyanide peak is also visible in the chromatogram. At these very low concentrations some of the Au(I)–thiosulfate complex is converted to Au(I)–cyanide by the cyanide impurities from the acetonitrile in the mobile phase.<sup>26</sup>

### Speciation of Gold in Environmental Water Samples.

Six water samples from a range of sites including mine dewatering ponds (D), mine monitoring bores (samples M1, M2, and M3), mine tailings (T) and a hypersaline surface water (L) were analyzed using the developed method. Four of the samples (M1, M2, M3, and D) contained  $[\text{Au}(\text{CN})_2]^-$  (Figure 3); gold was not detected in sample T. Unexpectedly a peak

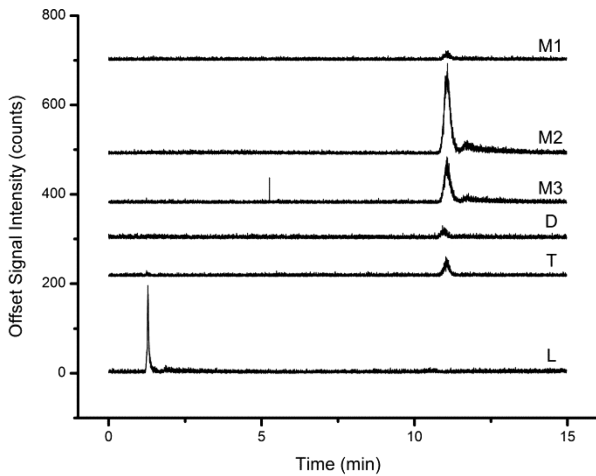


Figure 3. Water samples associated with gold mines; other conditions as Figure 2.

consistent with an Au(III) complex was observed in the Lake Way sample (L) (Figure 3). The level of  $[\text{Au}(\text{CN})_2]^-$  was

determined for samples M1, M2, M3, and D1 as discussed below. Further investigations into the nature of the possible Au(III) peak from L is discussed separately.

**Detection and Significance of the  $[\text{Au}(\text{CN})_2]^-$  Complex.** The concentrations of  $[\text{Au}(\text{CN})_2]^-$  in M1, M2, M3, and D were determined with HPLC-ICP-MS by multiple standard additions of a  $\text{K}[\text{Au}(\text{CN})_2]$  standard. Matrix matching via standard additions was chosen for the quantification in order to allow for enhancement of the signal that resulted from other components in the sample matrix. Trace levels of Au(I)–cyanide ( $[\text{Au}(\text{CN})_2]^-$ ) were detected (Table 3), at levels ranging from ~0.7 to 10.6  $\mu\text{g L}^{-1}$ . The accuracy of the method was estimated by determining the recovery of  $[\text{Au}(\text{CN})_2]^-$  in a spiked monitoring bore water sample from the Granites Gold Mine. The resultant linear regressions (SI, Figures S6 and S7) had 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  $\text{L}^{-1}$ , yielding a 110% recovery of the 7 mg  $\text{L}^{-1}$  spike.

Our direct analysis findings confirm Leybourne et al.'s<sup>6</sup> chemical speciation modeling, which attributed elevated gold levels in a drained gossan pile to formation of the  $[\text{Au}(\text{CN})_2]^-$  complex via reaction with the cyanide used to process the gossan for gold a decade ago. Previous studies of tailings dams have predominantly focused on the mobility of arsenic, mercury and other metal contaminants (i.e., Cu, Zn, Pb, Co, and Ni).<sup>31–34</sup> However, studies on the mobilization/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.<sup>6</sup> attributed the decreasing gold concentrations, further downstream from the gossan tailings pile, to Au(I)–cyanide reducing to nanoparticles).

The levels of  $[\text{Au}(\text{CN})_2]^-$  found were well below the weak acid dissociable (WAD) cyanide concentrations deemed safe for wildlife (below 50 mg  $\text{L}^{-1}$ ).<sup>35</sup> Furthermore,  $[\text{Au}(\text{CN})_2]^-$  is considered to be a strong acid dissociable complex, where only harsh acidic conditions will liberate free cyanide.<sup>36</sup> Thus, at these levels,  $[\text{Au}(\text{CN})_2]^-$  should not pose an environmental risk for the formation of free cyanide. It is important to note, however, that this assessment does not include any other cyanide complexes that may be present in these waters. The formation of strong complexes, such as  $[\text{Co}(\text{CN})_6]^{3-}$ , is a mechanism for cyanide stabilization,<sup>37</sup> and thus the formation and detection of  $[\text{Au}(\text{CN})_2]^-$  is a highly sensitive way to detect tiny amounts of free cyanide. As an example, only  $1 \times 10^{-17}$   $\mu\text{mol}$  of free  $\text{CN}^-$  would remain in solution if 0.005  $\mu\text{mol}$  of Au ( $1 \mu\text{g L}^{-1}$ ) was reacted with 0.015  $\mu\text{mol}$  of  $\text{CN}^-$  (SI, Figure S8).

The proximity of the sampling points to either tailings or the mine processes suggests that  $[\text{Au}(\text{CN})_2]^-$  may be due to anthropogenic cyanide (from leaching processes), rather than

Table 3. Concentrations of  $[\text{Au}(\text{CN})_2]^-$  Determined with HPLC-ICP-MS<sup>a</sup>

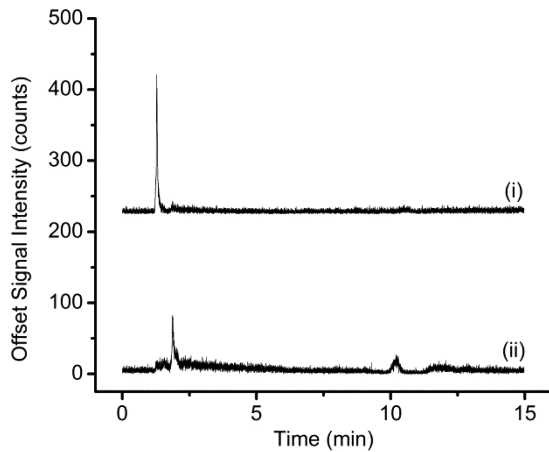
sites	$[\text{Au}(\text{CN})_2]^-$ ( $\mu\text{g L}^{-1}$ )	$[\text{Au}]$ ( $\mu\text{g L}^{-1}$ )	LOD ( $\mu\text{g L}^{-1}$ )	slope (counts ( $\mu\text{g L}^{-1}$ ) <sup>-1</sup> )	R <sup>2</sup>	ICP-MS total $[\text{Au}]$ ( $\mu\text{g L}^{-1}$ )
M1	1.5 ± 0.2	1.2 ± 0.1	0.10	52.32	0.9893	1.15 ± 0.01
M2	10.6 ± 0.4	8.4 ± 0.3	0.12	43.55	0.9976	13 ± 2
M3	9.2 ± 0.4	7.3 ± 0.3	0.10	50.51	0.9989	13.5 ± 0.7
D	0.7 ± 0.1	0.52 ± 0.09	0.08	61.07	0.9916	0.8 ± 0.2

<sup>a</sup>Limit of detection (LOD) =  $(\sigma_B/S)$ , where  $\sigma_B$  = standard deviation of the blank and  $S$  = slope.<sup>30</sup>

cyanide-producing plants or microorganisms. Hence, these results show that mineral explorers should be mindful of the sampling location when groundwater samples are collected and analyzed for total dissolved gold in order to develop regional vectors for gold mineralization.<sup>38,39</sup>

**Nature and Significance of the Au(III) Complex in the Lake Way Water.** Speciation analysis of the Lake Way surface water (L) shows that a Au(III) complex (such as  $[\text{Au}(\text{OH})_4]^-$ ) may be present; however, this Au(III) peak elutes with the void and may result from matrix effects on the background signal due to unretained components such as chloride in the sample.<sup>40</sup> Consequently, the mobile phase composition was readjusted to include 1% v/v of (1 mM) hexadecyltrimethylammonium hydroxide (HDTMA-OH). Consistent with the report of Horvath et al.<sup>41</sup> incorporation of this larger chain ion-pair agent shifted the retention times of the Au(III)-chloro-hydroxy species so that they eluted later (SI, Figure S9)<sup>41</sup> while background peaks due to sodium chloride remained with the void. Thus, the Au(III) peaks were shifted from coeluting unretained matrix components.

Reanalysis of the Lake Way water sample (L) using the modified mobile phase showed a peak at 1.9 min (Figure 4).



**Figure 4.** Comparison of the retention of the Au(III) complex in the Lake Way sample in (i) original mobile phase (as in Figure 1) and (ii) modified mobile phase: 6:17.5 v/v isopropanol: acetonitrile, 1 mM ion-pairing agent (99:1 v/v TBA-Cl: HDTMA-OH), 5 mM  $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ , pH 7.

complex in this sample. The concentration of the Au(III) complexes ( $\sim 0.4 \mu\text{g L}^{-1}$ ) was calculated by the area under the curve. In addition to the peak at 1.9 min, the Lake Way chromatogram contains a small peak (just visible above the background noise) at 10.2 min followed by a noticeable dip (or disturbance) in the signal. This suggests that the Lake Way sample may also contain  $[\text{Au}(\text{CN})_2]^-$ . Given the very low levels of gold in this sample, contamination by  $\text{CN}^-$  from the mobile phase is difficult to exclude (see the above Method Development section); even in the case of such a contamination, however, it appears that both Au(I) and Au(III) complexes coexist in this water.

In order to identify possible Au-complexes, the hydrochemical 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. (Tables 4 and 5).

The Lake Way water had high concentrations of dissolved salts such as  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2+}$ , which may have been responsible for the unretained matrix peak in Figure 4. The pH of the water was near-neutral ( $\sim 7.64$ ). Interestingly, the Lake Way water contained elevated concentrations of manganese ( $\sim 2.3 \text{ mg L}^{-1}$ ) when compared to typical reported values. Dissolved manganese in natural waters can range from  $10 \mu\text{g L}^{-1}$  to  $>10 \text{ mg L}^{-1}$ , but is generally below  $0.2 \text{ mg L}^{-1}$ .<sup>42</sup> Distribution of species calculations suggest that this level of  $\text{Mn}^{2+}$  in the Lake Way water is stable under mildly reducing conditions ( $\log f\text{O}_{2(\text{g})} \leq -22$ ; 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.).<sup>43–45</sup> Consequently, the high concentration of  $\text{Mn}^{2+}$  in the Lake Way water (from the reduction of manganese oxides) may explain the presence of Au(III) in near-neutral waters. It has been reported by a number of authors that manganese may be able to oxidize and mobilize gold in the environment;<sup>46–49</sup> however, this process has only been demonstrated under acidic conditions, where the speciation gold was not directly measured.<sup>50,51</sup> To our knowledge, the effect of manganese minerals on the speciation of Au in mild (neutral pH) aqueous conditions has not been studied. Therefore, further work investigating the effect of manganese on the speciation of gold under less extreme conditions is required.

The results of the water analysis (Tables 4 and 5) were used for thermodynamic modeling to assess the possible Au-complexes in the Lake Way sample. Figure 5 (A) shows the solubility and equilibrium speciation of gold in Lake Way water

**Table 4. Geochemical Analysis of the Lake Way Water<sup>a</sup>**

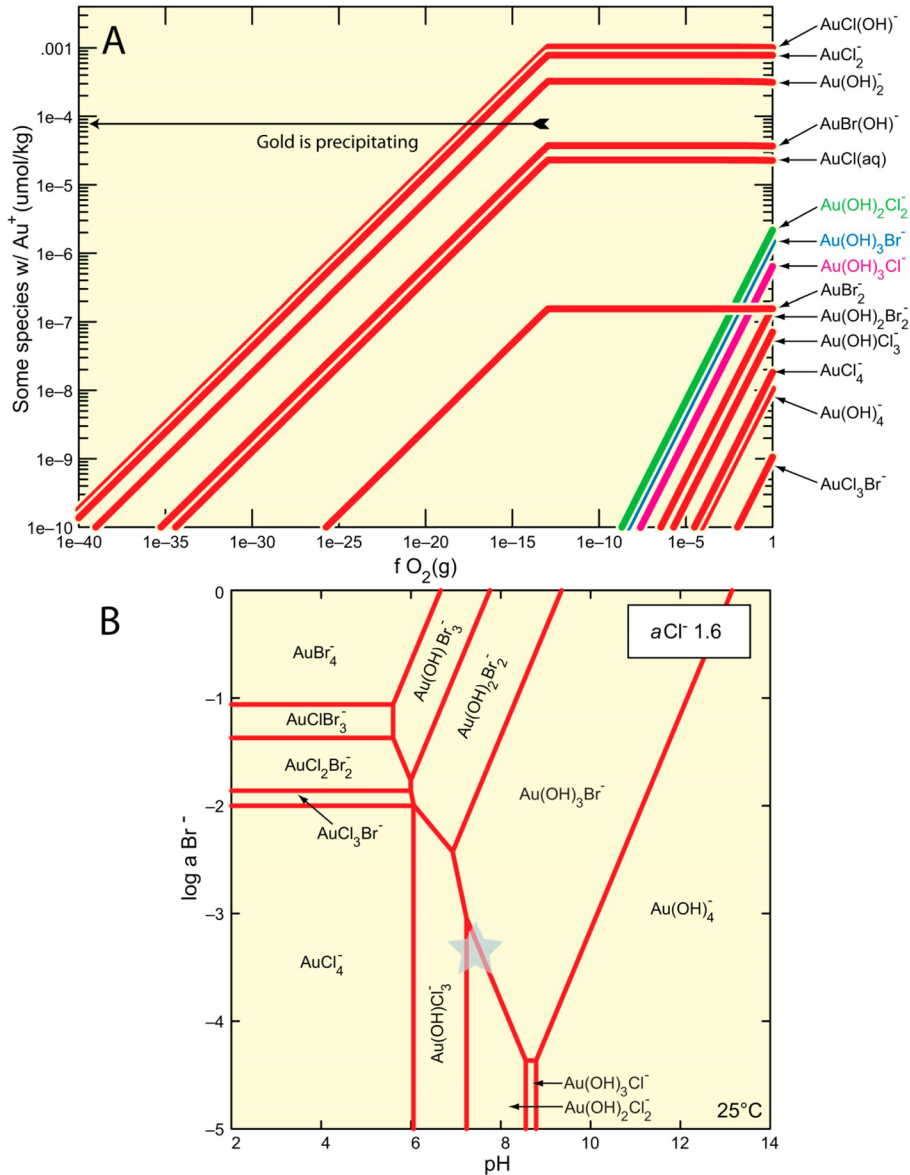
sample	pH	E.C.	NH <sub>4</sub> -N	NO <sub>x</sub> -N	TN	total alkalinity	DC	IC	DOC			
		dS m <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	meq L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>			
detection limits		0.01	0.005	0.005	0.1	0.1	0.5	0.1	0.5			
Lake Way	7.64	135.3	4.747	0.415	2.4	0.6	20.5	7.5	13.0			
sample		<sup>b</sup> Cl <sup>-</sup>	<sup>b</sup> Br <sup>-</sup>	<sup>b</sup> NO <sub>3</sub> <sup>-</sup>	<sup>b</sup> SO <sub>4</sub> <sup>=</sup>	<sup>c</sup> Ca	<sup>c</sup> K	<sup>c</sup> Mg	<sup>c</sup> Na	<sup>c</sup> S	<sup>c</sup> Si	<sup>c</sup> Sr
		mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>
detection limits	0.05	0.05	0.05	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.05
Lake Way	96 000	53	<20	41 000	327	5680	8130	49 700	8560	<5.0	7.08	

<sup>a</sup>pH, electrical conductivity (E.C.), ammonia-nitrogen ( $\text{NH}_4\text{-N}$ ), the sum of nitrate- and nitrite-nitrogen ( $\text{NO}_x\text{-N}$ ), nitrite-nitrogen ( $\text{NO}_2\text{-N}$ ) total nitrogen (TN), total alkalinity, dissolved carbon (DC), inorganic carbon (IC), dissolved organic matter (DOC), and major anions. Notes:  $\text{NO}_2\text{-N} < 0.005 \text{ mg L}^{-1}$ . <sup>b</sup>Elements analyzed by ion chromatography;  $\text{F}^- < 2 \text{ mg L}^{-1}$ . <sup>c</sup>Elements analyzed by ICP-OES; Al, As, Cd, Co, Cu, Ni, Pb, Se, Zn  $< 0.5 \text{ mg L}^{-1}$ ; B, Fe, P, Sb  $< 1 \text{ mg L}^{-1}$ .

Table 5. ICP-MS Analysis of the Groundwater from Lake Way Water<sup>a</sup>

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
Lake Way	2300	<10	600	8.4	5	20	<1	<20	<30	12	4	1.4	<2	0.4	2	<0.5	8.05

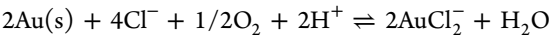
<sup>a</sup>Notes: The following elements were analyzed but found to be below detection limit: Sc, V, Y, Pd, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Re, Pt, Pb < 0.2  $\mu\text{g L}^{-1}$ ; Zn < 1  $\mu\text{g L}^{-1}$ ; Ag < 0.1  $\mu\text{g L}^{-1}$ .



**Figure 5.** 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 star marks the pH and log  $a[\text{Br}^-]$  of the Lake Way sample).

(Tables 4 and 5) as a function of oxygen fugacity. Gold becomes supersaturated at  $\log f_{\text{O}_2(\text{g})}$  lower than  $10^{-12}$  bar; this suggests some disequilibrium between Au and Mn, since Mn becomes supersaturated at  $\log f_{\text{O}_2(\text{g})}$  above  $10^{-22}$  bar. The modeling also confirms that the presence of Au(III)-complexes is inconsistent with equilibrium thermodynamics. The Au(I) complexes  $[\text{AuCl}(\text{OH})]^-$ ,  $[\text{AuCl}_2]^-$ ,  $[\text{Au}(\text{OH})_2]^-$ ,  $[\text{AuBr}(\text{OH})]^-$ ,  $\text{AuCl}(\text{aq})$ , and  $[\text{AuBr}_2]^-$  are predominant, but Au(III) complexes are unstable even at overoxygenated

conditions in the Lake Way water ( $f_{\text{O}_2(\text{g})} = 1$  bar). Similarly, modeling by Gray and Pirlo<sup>5,39</sup> on saline waters from Tunkillia and from the Yilgarn Craton, Australia, predicted the speciation of gold to be gold(I)-halides (i.e.,  $\text{AuCl}_2^-$ ,  $\text{AuI}_2^-$ ). According to the Gray and Pirlo,<sup>5</sup> the dominant mechanism for the mobilization of gold in  $\text{Cl}^-$  rich waters is





In an effort to identify the Au(III) species in Lake Way, only Au(III) ions were modeled in the presence of Br<sup>−</sup> and Cl<sup>−</sup> ions (Figure 5 (B)). At pH 7.9 and the calculated Br<sup>−</sup> and Cl<sup>−</sup> activities, the major gold species are predicted to be [Au(OH)<sub>2</sub>Cl<sub>2</sub>]<sup>−</sup>, [Au(OH)<sub>3</sub>Br]<sup>−</sup> and [Au(OH)<sub>3</sub>Cl]<sup>−</sup> (indicated by the yellow star). The retention time of the broad peak in the Lake Way chromatogram (Figure 4 (ii)) is consistent with these species.

For the first time, direct speciation analyses of environmental waters shows that the mobility of gold is controlled by kinetic factors rather than by thermodynamic equilibria. Where the [Au(CN)<sub>2</sub>]<sup>−</sup> complex predominates, Au mobility is controlled by the presence of a metastable ligand, cyanide. Indeed, the formation of a strong complex with Au(I) is likely to explain the survival of trace amounts of cyanide in the groundwater away from the anthropogenic source; such an effect was demonstrated for the weaker Co(II)–cyanide complexes by Johnson et al.<sup>37</sup> In the Lake Way water (L), a large amount of Au is present as a Au(III) complex (most likely a mixed hydroxide–halide complex). The oxidation of gold to Au(III) is clearly kinetically controlled; although a Mn pathway is possible, the exact process remains unknown. The presence of Au(III) in natural waters may be very important, because Au(III) complexes are highly soluble, and display far higher toxicity to micro-organisms than Au(I) complexes.<sup>52</sup> The elevated toxicity likely drives the formation of gold-detoxifying biofilms that catalyze the biomineralization of spheroidal nanoparticulate gold, hence accelerating the biogeochemical cycling of gold.<sup>22</sup>

Previous experiments that form the basis for the thermodynamic and kinetic models used to understand how gold exists in the environment were undertaken at high concentrations and should now be revisited at environmentally relevant concentrations. Such studies include gold solubility and speciation in the chloro-hydroxyl system,<sup>8,53,54</sup> the Au(I)–sulfur system,<sup>55</sup> the Au–humic acid system,<sup>56</sup> and the interaction between Au and Mn minerals over a range of pH.<sup>46,47,49,50,57–59</sup>

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental method, HPLC method development, spike-and-recovery analysis plots and chromatograms from the hydrolysis and ligand exchange experiments and the modified mobile phase. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

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## ■ ABBREVIATIONS

tetrabutylammonium chloride (TBA-Cl)  
hexadecyltrimethylammonium hydroxide (HDTMA-OH)

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