# 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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**May 2013**

# 4. Manganese and Gold

## 4.1 Introduction

In Chapter 3, elemental analysis of the Lake Way water, containing Au(III), revealed high levels of Mn (2.3 mg $L^{-1}$). As discussed, these unusually high levels are thought to result from the reduction and dissolution of manganese oxides as described by Howe [174]. This chapter explores possible links between Mn and the mobilisation of gold in the environment under circumneutral conditions like the Lake Way water.

### 4.1.1 Mn in the environment

Manganese (Mn) makes up 0.1% of the Earth's crust, with background levels of Mn in soils ranging from <1 to 4000 mg/kg dry weight [174]. In natural waters, dissolved manganese can range from 10 μg $L^{-1}$ to >10 mg $L^{-1}$, but are usually below 0.2 mg $L^{-1}$ [174]. In the aquatic environment, Mn exists in two main oxidation states: Mn(II) and Mn(IV) [174]. Mn(II) salts are generally water-soluble and present in anaerobic, reducing or acidic waters (<pH 5). Alternately, Mn(IV) is usually observed as an insoluble manganese oxide ($MnO_2 \bullet xH_2O$ and sometimes in colloidal form), and is the dominant form above ~pH 5 [191-193]. In soils, Mn is generally found as a manganese oxide in one of three oxidation states, Mn(II), Mn(III) and Mn(IV) [194]. Common manganese oxides include birnessite, hollandite, pyrolusite, todorokite and lithiophorite [195]. Although the pathway between the different oxidation states are driven by both biotic and abiotic processes [196-200], the majority of Mn-oxides in nature arise from the oxidation of Mn(II) by bacteria and fungi [201]. Other forms of manganese in the environment include organic complexes such as MMT (methylcyclopentadienyl manganese tricarbonyl) and binuclear complexes of Mn(II), (III), and (IV). MMT is a common fuel additive that is an environmental contaminant [202], while binuclear Mn complexes are commonly produced bacterial enzymes involved with the protection of living cells against oxidative stress, the photosynthetic oxidation of water, and the reduction of ribonucleotides [203-206].

Mn-oxides are known to be very reactive and to oxidise many ions. These include Fe(II)→Fe(III), As(III)→As(V), Cr(III)→Cr(VI), Pu(IV)→Pu(VI), Co(II)→Co(III) and Ce(II)→Ce(IV) [207, 208]. In fact, Mn-oxides are the only known oxidiser of Cr in soils [209, 210]. Several studies have investigated the Mn-oxide-related oxidation of metallic ions, which two possible modes of reaction are proposed:

1) Microbially-mediated co-oxidation of the metallic ion with Mn(II) ions during the biogenic formation of Mn(III/IV) oxides [208],
2) Adsorption of the metallic ion onto a manganese oxide surface, followed by surface-mediated oxidation of the metallic ion and formation of $Mn^{2+}$ [176, 177, 211-214].

This Mn-oxide-related oxidation of metallic ions has been observed under acid, near neutral and alkaline conditions. Certain oxomanganese complexes are also involved in the photosynthetic oxidation of water [204], however, the effect of oxomanganese complexes on metal ions in the environment is not fully understood.

### 4.1.2 Mn reacting with gold

There are very few studies on the interaction of Mn and gold in environmental waters. Goldschmidt [179] proposed strongly oxidising ions, such as Mn(IV) or Fe(III), may be responsible for the weathering of gold, however evidence for this was not presented. This hypothesis reflects the work of Krauskopf [178], who used Latimer and Hildebrand's [215] standard electrode potentials in acid solutions to predict that gold may be oxidised by $MnO_2$ in acid solution (provided that $Cl^-$ is present) to form $AuCl_4^-$:

$$\mathrm{Au} + 4\mathrm{Cl}^- = \mathrm{AuCl}_4^- + 3\mathrm{e}^- \quad (-1.00)$$
$$\mathrm{Mn}^{2+} + 2\mathrm{H_2O} = \mathrm{MnO_2} + 4\mathrm{H}^+ + 2\mathrm{e}^- \quad (-1.28)$$

In 1911 Emmons [2] suggested that the oxidation of gold occurs in oxidising surface waters that are cold, dilute in minerals and acidic, where the presence of manganese oxides oxidises ferrous sulfate to ferric sulfate. The presence of Fe(III) was thought to prevent the precipitation of gold-chloride solutions until transport into deeper zones, where conditions are usually less acidic and the precipitation of both gold and manganese occurs [2]. Both Emmons [2] and Boyle [1] surmised that manganese oxides were able to oxidise gold into a soluble complex (such as Au(III)-chloride) if sulfuric acid was present to produce free chlorine to render gold as a mobile chloride complex:

$$\mathrm{H_2SO_4} + 2\mathrm{NaCl} \rightarrow 2\mathrm{HCl} + \mathrm{Na_2SO_4}$$
$$4\mathrm{HCl} + \mathrm{MnO_2} \rightarrow \mathrm{MnCl_2} + 2\mathrm{H_2O} + \mathrm{Cl_2}$$
$$\mathrm{Au} + \mathrm{Cl_2} \rightarrow \text{Soluble complexes such as } [\mathrm{AuCl_4}]^-$$

Two other previous studies examining the reactions of Mn oxides with gold have been undertaken in acidic conditions. Rickard [181] solubilised all the gold in a gold-rich ore containing manganese oxides, through treatment with ferric sulfate, sodium chloride and a little sulfuric acid. Similarly, Cloke and Kelly [180] found a sheet of gold was slightly solubilised (0.8 mg of gold) when in contact with acidic chloride solutions (0.5 M $H_2SO_4$ and 0.1 M NaCl), which had been filtered through crushed pyrolusite ($MnO_2$). Whilst these studies demonstrate the mobilisation of gold into aqueous solution, neither identified the gold oxidation state nor used environmentally relevant conditions. A third study, performed under alkaline conditions, found manganese solutions were capable of precipitating gold-chloride solutions [216]:

$$2\mathrm{AuCl_3} + 3\mathrm{MnCl_2} + 12\mathrm{KOH} = 2\mathrm{Au} + 3\mathrm{MnO_2} + 6\mathrm{H_2O} + 12\mathrm{KCl}$$

Manganese oxides have also been shown to adsorb Au(III) ions, at pH 6–9, and spontaneously reduce some of the Au(III) ions adsorbed [217-219]. There are no reports of oxomanganese complexes reacting with gold.

Despite these early studies, there has been no systematic study on the reaction of manganese oxides with gold in aqueous solutions. Additionally, whilst previous work provides evidence for gold solubilisation, the oxidation state of the gold was unable to be determined. Our developed method provides this capability.

## 4.2 Study Scope

Presented in this chapter are preliminary studies investigating the ability of various manganese oxides (pyrolusite, birnessite, tokodorite, cryptomelane, lithiophorite/ vernadite/ goethite, chalcophanite/ hetaerolite and coronadite) and manganese complexes (Mn-1,4,7-triazacyclononane, $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2](NO_3)_3$, (bpy = 2,2’-bipyridyl)) to oxidise Au(I) or Au(0) to form aqueous Au(III) under non-acidic, surface conditions (i.e. the Lake Way water). The study of synthetic analogues (including pyrolusite and potassium permanganate) are also important, as they can be synthesised without the trace elements found in the biogenic, or abiotic minerals [220]. Changes to the speciation of gold are monitored by the HPLC-ICP-MS method developed in Chapter 2.

# 4.3 Experimental

## 4.3.1 Reagents and Standards

The chemicals used in this study are shown in Table 2-1. Unless otherwise specified ~18 MΩcm deionised water (Millipore, Australia) utilised for the preparation of aqueous solutions.

**Table 4-1 The chemicals used in this study.**

| Chemical | Supplier | Grade | Concentration/Purity |
|---|---|---|---|
| Acetonitrile | Ajax Finechem | HPLC | 99.7% |
| Disodium orthophosphate phosphate anhydrous powder | Scharlau | Analytical | >99.0% |
| Gold powder, spherical, 3–5.5 μm | Alfa Aesar | Not stated | 99.96+% |
| Gold standard in 2% HCl | Choice Analytical | Analytical | 1000 mg $L^{-1}$ |
| High purity HCl | Scharlau | Analytical | 37% |
| Isopropanol | Merck | HPLC | Not stated |
| Orthophosphoric acid | Ajax Finechem | Analytical | 85% |
| Potassium permanganate | Chem-Supply | Analytical | 99+% |
| Sodium gold(I) thiosulfate hydrate | Alfa Aesar | Reagent | 99.9 % (35.69% Au) |
| Sodium dihydrogen phosphate anhydrous | Chem-Supply | Analytical | >98% |
| Sodium chloride | Ajax Finechem | Analytical | >99% |
| Tetrabutylammonium chloride hydrate (TBAC) | Sigma-Aldrich | Reagent | 98% |
| Triton™ X-100 | Sigma-Aldrich | Analytical | 100% |

## 4.3.2 Manganese compounds

The gold oxidation experiments were carried out with the manganese compounds listed in Table 4-2. The synthetic minerals were provided by Dr. Leone Spiccia, Monash University and the natural minerals were from the South Australia Museum Mineral Collection. The natural samples were analysed with XRD to confirm that they were manganese minerals by Dr. Barbara Etschmann from the South Australian Museum (Appendix C).

**Table 4-2 List of synthetic and natural manganese compounds in this study.**

| Mn-oxide | Formula | Locality | Source | S.A. Museum Registration Number |
|---|---|---|---|---|
| Synthetic Pyrolusite | $MnO_2$ | Australia | Monash University | N.A. |
| Commerical $MnO_2$ | $MnO_2$ | | | |
| Mn-1,4,7-Triazacyclononane (Mn-TACN) | $Mn^{4+}(C_6H_{12}(NH)_3)$ | | | |
| di-μ-oxo-bpy-bridged $Mn^{III}Mn^{IV}$ complex (bpy = 2,2'-bipyridyl) | $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2](NO_3)_3$ | | | |
| Birnessite | $(Na,Ca,K)(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5(H_2O)$ | 25 km S, Condermine, QLD | South Australian Museum | G17606 |
| Lithiophorite/vernadite/ goethite | $(Al,Li)Mn^{4+}O_2(OH)_2$/<br>$(Mn^{4+},Fe^{3+},Ca,Na)(O,OH)_2.n(H_2O)$/<br>$Fe^{3+}O(OH)$ | Mt Davis, WA | | G18130 |
| Todorokite, | $CaMn^{2+}(CO_3)_2$ | Broken Hill, NSW | | G13911 |
| Cryptomelane | $K(Mn^{4+},Mn^{2+})_8O_{16}$ | Blinman, SA | | G7678 |
| Chalcophanite/ hetaerolite | $(Zn,Fe^{2+},Mn^{2+})(Mn^{4+})_3O_7 \cdot 3(H_2O)$/<br>$Zn(Mn^{3+})_2O_4$ | Reaphook Hill, SA | | G31991 |
| Pyrolusite | $MnO_2$ | Oraparina, SA | | G22723 |
| Coronadite | $Pb(Mn^{4+}, Mn^{2+})_8O_{16}$ | Iminer Mine, Morocco | | G30226 |

### 4.3.3 Oxidation experiments procedure

Unless otherwise specified, all reactions were conducted in closed polypropylene containers (Techno Plas, Australia) kept stirring in the dark prior to analysis. Before HPLC-ICP-MS analysis, 50 μL of the solution was withdrawn from the reaction vessel, diluted to 1 mL with water (20-fold dilution) and syringe-filtered through a 0.45 μm PVDF filter (Kinesis, Australia). The HPLC-ICP-MS method is detailed in Chapter 2.

#### *Natural and Synthetic Manganese Oxides*

1 mL of Au(I)-thiosulfate (100 mg $L^{-1}$ Au) was added to 1 mL of NaCl (1 M $Cl^-$) and an appropriate amount of Mn-oxide, so the final concentrations were ~0.0001 M Mn-oxide and 0.1 M $Cl^-$ when made up to 100 mL with water. The natural and synthetic manganese oxides tested are listed in Table 4-2 was trialled.

### *Kinetic experiments*

The oxidation of Au(I) and Au(0) by $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2](NO_3)_3$ and potassium permanganate were monitored over a day. The reactions were prepared as stated above, and 5 mg of powdered gold, 3.5 – 5 µm, (Alfa Aesar, U.K.) was used in the Au(0) experiments. The solutions were sampled at t = 0, 1, 2, 3, 4, 5, 6, 7, 12 hours and at 1 day. For samples under argon, the headspace of the solutions were sparged with argon, degassed by a sonicator and sparged a second time.

## 4.4 Results and Discussion

### 4.4.1 Oxidation of Au(I)

*Natural Manganese Minerals*

Preliminary studies investigating the oxidative power of natural manganese oxide minerals were conducted with Au(I) instead of Au(0) to ensure maximum contact between Au and Mn. Au(I)-thiosulfate was chosen instead of Au(I)-cyanide, because the latter is known to be very stable in solution. In order to ensure a chloride source was present, 0.01 M of sodium chloride was also added to the mixture. At this concentration of sodium chloride there are chloride ligands to stabilise any Au(III)-complexes that may form, however, not enough to cause any matrix interferences in the ICP-MS. All solutions (~0.0001 M manganese oxide with 1 mg $L^{-1}$ Au(I)-thiosulfate and 0.01 M sodium chloride) were prepared using deionised water and used as is. Under these conditions the manganese oxide is in excess by 20 times to the gold. No pH adjustment was undertaken to reduce matrix complexities affecting the measurement. Sample pH after analysis was measured to range from 5.4 to 9.3, depending on the mineral (Table 4-3). At these pH values, Mn is sparingly soluble and as such the reactions were left stirring with magnetic stirrer bars before analysis.

**Table 4-3** **The pH values of the natural Mn-oxide and Au(I)-thiosulfate reactions.** *Au(I)-thiosulfate ([Au]) = 1 mg $L^{-1}$), 0.01 M $Cl^-$, and ~0.0001 M of Mn-oxide.*

| Manganese oxide | pH |
|---|---|
| Birnessite (G17606) | 5.4 |
| Lithiophorite/vernadite/goethite (G18130) | 8.8 |
| Todorokite (G13911) | 6.2 |
| Crytomelane (G7678) | 9.3 |
| Chalcophanite/hetaerolite (G31911) | 8.1 |
| Pyrolusite (G22723) | 8.5 |
| Coronadite (G30226) | 7.9 |

Rather than showing each individual measurement, the chromatograms of the solutions after stirring for one day are shown in Figure 4-1 (A) and 3 months (B) respectively. As can be seen, there was no evidence of the formation of Au(III)-chloride in any of these samples. A plot of peak area of the Au(I)-thiosulfate peak versus reaction time is shown in Figure 4-2. It is evident from this plot that the peak area of Au(I) thiosulfate decreases in all samples over time, however, the rate of the decrease differs markedly between samples, with a rapid drop in peak intensities observed for Au(I) thiosulfate in the presence of lithiophorite/ vernadite/ goethite and pyrolusite (Figure 4-2 (i), and (vi)). The decrease in the Au(I) peak intensity is likely to result from two factors. Firstly, the adsorption of the gold complexes onto the Mn-oxides and goethite is well documented and may be followed by precipitation of the gold [217, 218, 221]. Secondly, the reduction in peak intensity may be due to adsorption of the

Au(I)-thiosulfate on to plastic sample container surfaces. This theory was tested by examining the concentration of two Au(I) stock solutions (a 50 µg $L^{-1}$ stock and a 1000 µg $L^{-1}$) after short-term storage in plastic in the dark. After 11 days, the gold concentration of the former stock solution had decreased by 27% and the latter by 5%. These results show that can Au(I)-thiosulfate gradually adsorb onto plastic (or fall out of solution) over time. The increased rate of Au(I)-thiosulfate removal seen in Figure 4-2 (i), and (vi)) is likely due to the adsorption onto mineral surface.

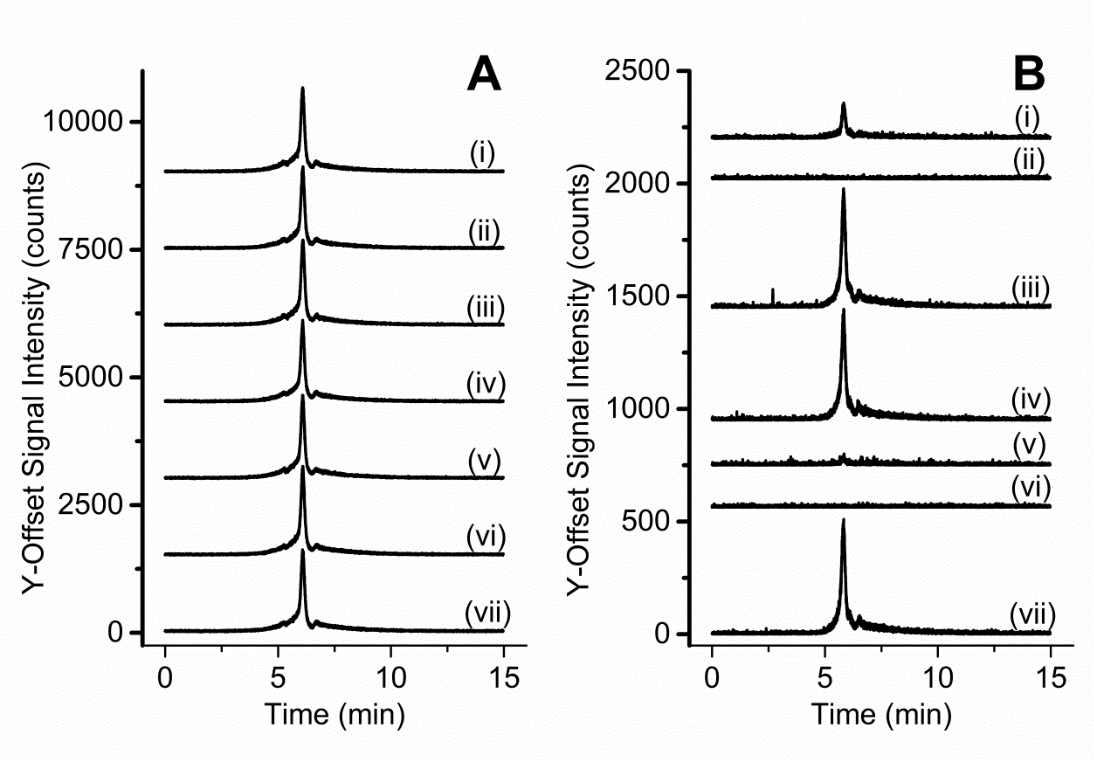

**Figure 4-1** **Effect of various Mn(III/IV) oxides on Au(I)-thiosulfate.**

*Chromatograms show Au(I)-thiosulfate peaks at 5.8 minutes after (A) one day and (B) three months in mixtures of 1 mg* $L^{-1}$ *Au(I)-thiosulfate, 0.1 M* $Cl^-$ *and ~0.0001 M (i) birnessite (G17606), (ii) lithiophorite/ vernadite/ goethite (G18130), (iii) kutnahorite (G13911), (iv) crytomelane (G7678), (v) chalcophanite/hetaerolite (G31991), (vi) pyrolusite (G22723), and (vii) coronadite (G30226); The samples were diluted 20x before analysis; Chromatograms are y-offset by 1500 counts. Mobile phase: 6: 17.5 v/v isopropanol: acetonitrile, 1 mM TBAC, 5 mM* $NaH_2PO_4/Na_2HPO_4$*, pH 7.*

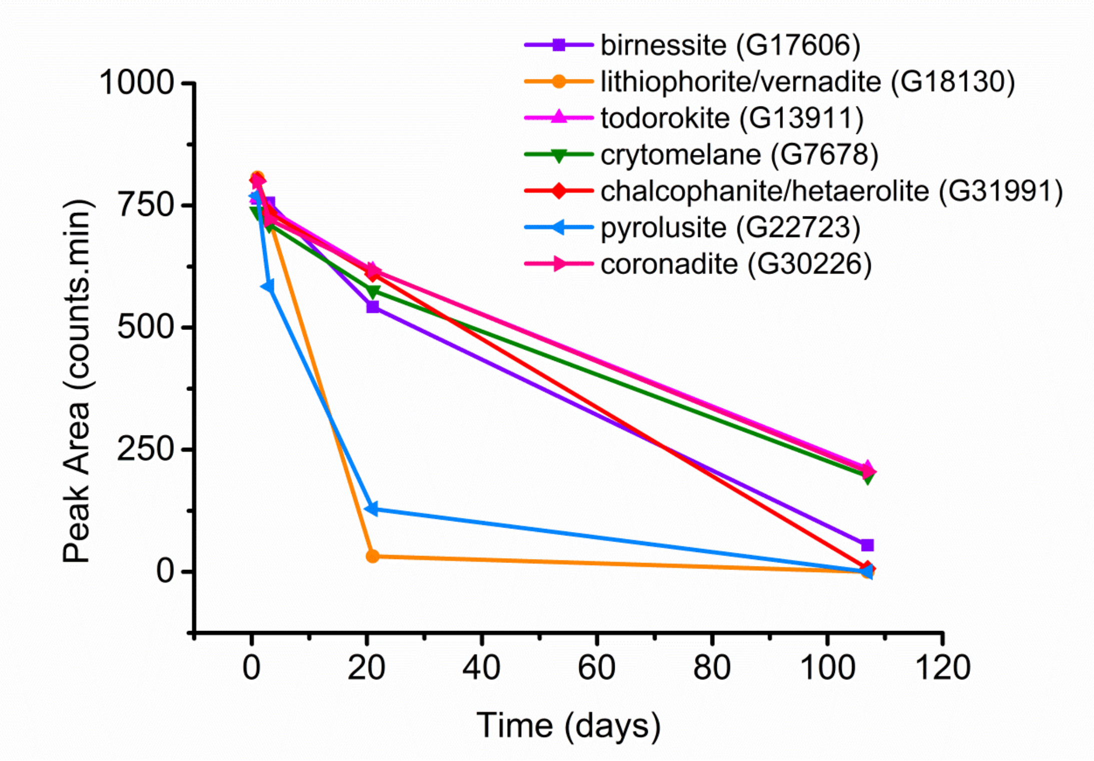

**Figure 4-2** **Effect of various Mn minerals on Au(I)-thiosulfate peak area over time.**

*Plots show a greater rate of decrease in peak area with the lithiophorite/ vernadite/ goethite (G18130) and pyrolusite (G22723) reactions.*

The formation of aqueous Au(III) was not observed with natural manganese oxides after three months, under non-acidic conditions. Au(III) complexes may have formed and remained bound on the mineral surfaces, however, further work with surface analysis techniques (i.e. scanning electron microscopy or x-ray absorption spectroscopy) is required to verify this and was outside the scope of this chapter. The purity of the manganese oxides may also have affected the potential oxidation of Au(I)-thiosulfate. XRD analysis showed the natural minerals obtained were often found in a mixture with other minerals (Appendix C). The accompanying minerals were often quartz, calcite and goethite. In order to reduce this source of uncertainty, synthetic manganese oxides were subsequently tested.

### *Synthetic manganese oxides*

Due to previous reports of their oxidative powers on other metallic ions [177, 209, 222-225], synthetic pyrolusite manganese dioxide ($MnO_2$), and potassium permanganate ($KMnO_4$) were chosen for oxidation experiments with Au(I)-thiosulfate. Whilst not normally present in the environment, $KMnO_4$ was chosen because it is readily available, cheap and has known redox activity. Furthermore, unlike the other synthetic manganese oxides, potassium permanganate is soluble in water. The manganese complexes, Mn-1,4,7-triazacyclonane (Mn-TACN), $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ (bpy = 2,2'-bipyridyl) were also trialled because the former is a known catalyst for oxidation [226], and the latter is a binuclear oxomanganese complex that is a heterogeneous catalyst to evolve oxygen from water [227]. It has been extensively studied as a model for the oxygen-evolving Photosystem (II) enzyme (splitting of water) [228-230]. Other conditions remained the same as the previous experiments with the natural minerals.

The speciation of gold after twenty-three days of stirring with the synthetic manganese oxides is shown in Figure 4-3. As can be seen (Figure 4-3 (iv) and (v)), the oxidation of Au(I)-thiosulfate by $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)2]^{3-}$ and potassium permanganate results in the appearance of a new peak that has a retention time that is consistent with Au(III) chloride/hydroxide. As shown in the inset, this occurs within a day of mixing. The remaining synthetic Mn sources tested, synthetic pyrolusite, commercial $MnO_2$ and Mn-TACN complex did not result in a change in the Au(I)-thiosulfate peak after stirring for 23 days.

Then, when comparing the chromatograms for Au(I)-thiosulfate + $KMnO_4$ and Au(I)-thiosulfate + $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)2]^{3-}$, it is evident that Au thiosulfate is not detectable in either reaction mixtures after one day. Continued mixing resulted in an increase in the peak intensity of the new Au(III) peaks for each mixture. This indicates that the reaction mechanism may proceed via a multistep process where a solid intermediate is formed. Additionally, the Au oxidation products from $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ and potassium permanganate have different retention times (1.3 and 1.6 minutes respectively). The Au(III)-potassium permanganate peak had also formed a double peak, which was accompanied by smaller shoulder peaks Figure 4-3 (v). This indicates that the Au(III)-complexes formed from each reaction are different. The potassium permanganate peaks fall within the typical range of retention times for the Au(III)-chloride-hydroxide complexes (between 1.6 and 3.4 minutes), however, it is possible that the $KMnO_4$ and $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)2]^{3-}$ reactions formed Au(III)-manganese oxide complexes (there have been reports of various Au-Mn complexes and Au-Mn-O bonds) [219, 231]. Blank reactions containing no gold were also analysed at t = 0 and 1 day, to ensure the Au(III) peaks are indeed from the gold and not matrix effect peaks (Appendix D). Apart from the $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ reaction, which was at pH 4.68, the pH values of the reactions were at near neutral conditions, and are listed in Table 4-4. The lower pH in the $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ reaction may be due to the oxidation of water to form oxygen and hydrogen ions [227].

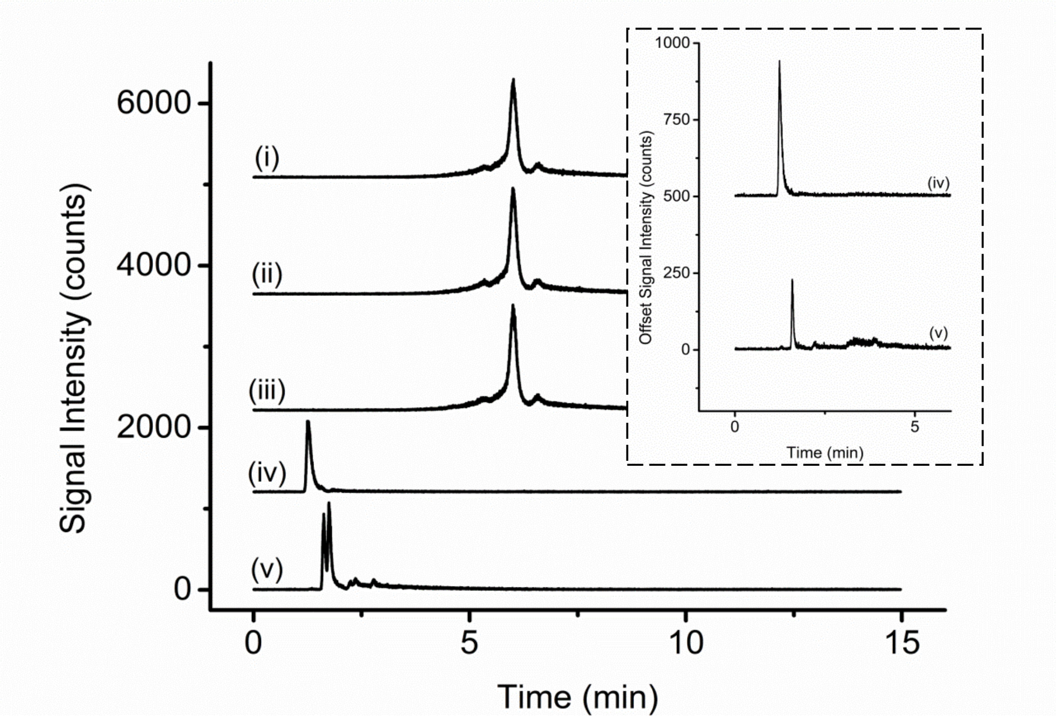

**Figure 4-3** **Effect of synthetic manganese compounds on Au(I)-thiosulfate after 23 days.** *Chromatograms of Au(I)-thiosulfate ([Au]) = 1 mg* $L^{-1}$*), 0.01 M* $Cl^-$*, and ~0.0001 M of (i) pyrolusite, (ii) commercial* $MnO_2$*, (iii) Mn-TACN, (iv)* $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ *and (v) potassium permanganate; Chromatograms are approximately y-offset at intervals of 1200 counts; chromatograms at t = 1 day are shown in the inset graph. The samples were diluted 20x before analysis; Other conditions as Figure 4-1.*

**Table 4-4** **The pH values of the Mn-oxide and Au(I)-thiosulfate reactions.**

*Au(I)-thiosulfate ([Au]) = 1 mg* $L^{-1}$*), 0.01 M* $Cl^-$*, and ~0.0001 M of Mn-oxide.*

| Mn-oxide | pH |
|---|---|
| Pyrolusite | 6.6 |
| $MnO_2$ | 6.7 |
| Mn-TACN | 7.0 |
| $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ | 4.7 |
| $KMnO_4$ | 6.9 |

### 4.4.2 Oxidation of Au(0)

In order to determine whether $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ or potassium permanganate could oxidise Au(0), these oxidation experiments were repeated with gold powder in place of Au(I)-thiosulfate. Figure 4-4 (iv) shows that after t = 1 day, $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ is the most reactive in oxidising Au(0) to Au(III). An intermediate Au(I) complex was not observed, indicating that the mechanism of oxidation either: 1) does not proceed via the formation of a soluble Au(I) compound, or 2) a Au(I) intermediate is formed, but is immediately/rapidly oxidised and thus is present at very low concentrations. There were small Au(III) and Au(I)-cyanide peaks in the potassium permanganate reaction (Figure 4-4 (v)). The Au(I) peak suggests that the oxidation of Au(0) to Au(III) by potassium permanganate goes through a Au(I) intermediate step (although the concentration of gold is so low that minimal cyanide impurities in the mobile phase can react with the gold, as discussed in Chapter 2, Section 2.4.9). ICP-MS analysis of a 0.01 M NaCl solution with Au(0) after stirring for one day showed that no gold was oxidised into solution in the absence of the binuclear oxomanganese compound.

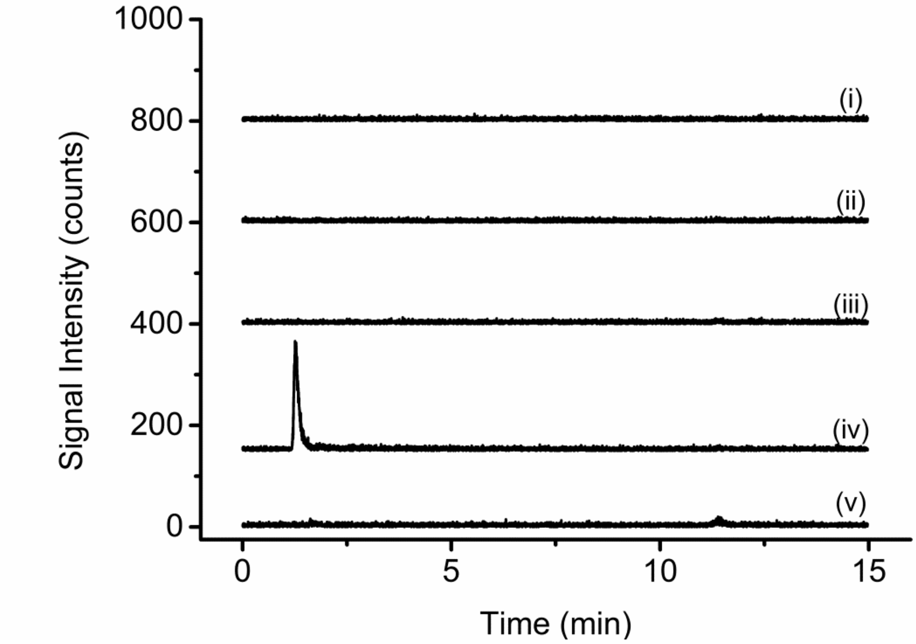

**Figure 4-4** **Effect of synthetic manganese oxides on Au(0), t = 1 day.**

*Chromatograms of 5 mg of gold powder ([Au]) = 1 mg* $L^{-1}$*), 0.01 M* $Cl^-$*, and ~0.0001 M of (i) pyrolusite, (ii) commercial* $MnO_2$*, (iii) Mn-TACN, (iv)* $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ *and (v) potassium permanganate; Other conditions as Figure 4-1.*

### 4.4.3 Kinetic Au(I) Oxidation Studies with Potassium Permanganate and $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$

Results in Section 4.4.1 showed evidence of the formation of a Au(III) complex being formed upon reaction with $KMnO_4$ and $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ with new peaks evident after a day. As the oxidation of Au(I) by $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ and potassium permanganate was quite rapid, these reactions were repeated and monitored with HPLC-ICP-MS over 24 hours. In order to verify the oxidation of Au(I) was from the manganese oxides and not oxygen in the air, a replicate set of reactions that were degassed with argon were also run for comparison. The oxidation reactions were sampled every hour for the first 7 hours, then at t = 12 hours and t = 1 day. Figure 4-5 shows the resulting chromatograms from potassium permanganate reacting with Au(I)-thiosulfate under both (A) atmospheric conditions and (B) under argon. The peak area for Au(I)-thiosulfate and the resultant oxidation products over time are plotted in Figure 4-6. It can be seen that the oxidation of Au(I)-thiosulfate by potassium permanganate follows similar steps for both conditions:

1. The Au(I)-thiosulfate peak decreases in intensity over the first few hours. During this time there is no evidence of a new Au peak.
2. After approximately 4 hours the Au(I) thiosulfate levels are below the detection limit of the system.
3. Around this time (3-4 hours) a small peak forms at 3.2 minutes. This peak is found in all subsequent chromatograms and its intensity does not change. This identity of this peak is uncertain
4. At around 5 hours a small double peak with a retention time that is consistent with Au(III) forms. This peak could correspond to Au(III)-chloride or Au(III)-manganese oxide peak.

Both the Au(III) complex and the unidentified complex only appear after the removal of Au(I)-thiosulfate from the solution, however, this removal of Au(I)-thiosulfate does not commence instantly upon mixing. This delay suggests that something else in the reaction system is undergoing a transition state, which then catalyses the removal of Au(I)-thiosulfate from solution. In previous studies, permanganate has been shown to undergo reduction to a Mn-oxide solid, then adsorb As(III) ions and oxidise them to As(V) [222, 223]. We propose that the $KMnO_4$ and Au(I)-thiosulfate undergoes a similar reaction pathway, where the majority of the Au(I) to Au(III) oxidation occurs on the surface of a manganese oxide colloid. The formation of the Au(III) complex occurs very slowly, while the unknown peak appears to be unchanged over this period. This suggests that the unknown peak is a steady state reaction intermediate complex, where its rate of formation (from the colloidal manganese surface) and rate of breakdown (to form the Au(III) complex) is equal. The unknown complex may either be a manganese bound Au(I) or Au(III) complex, however, further work (such as manganese speciation) will be necessary to identify the complex and confirm the hypothesised oxidation mechanism.

Interestingly, there was an initial formation of Au(III) upon beginning the reaction under air (Figure 4-5 (A), t = 0). Replicate experiments showed that this was consistent and not due to cross contamination on the chromatographic system. According to Lee *et al.* [222], the reduction of permanganate (Mn(VII) to a Mn(II/III/IV) oxide) can also catalyse the oxidation of some of the As(III) ions present. Therefore, the formation of the Mn solid is likely to do the same to some of the Au(I)-thiosulfate. This effect was not observed with the reaction under argon (Figure 4-5 (B), t = 0). It is thought that this could be due to two different reasons: 1) the absence of oxygen may have prevented the formation of these complexes, or 2) in the 10 minutes taken to deoxygenate the Argon reaction before the t = 0 sampling, the Au(III) complexes may have formed and precipitated out of solution. This initial Au(III) complex does not appear to be very stable and is no longer present after the first hour of mixing. This suggests that these Au(III) complexes are different to those formed that are formed later.

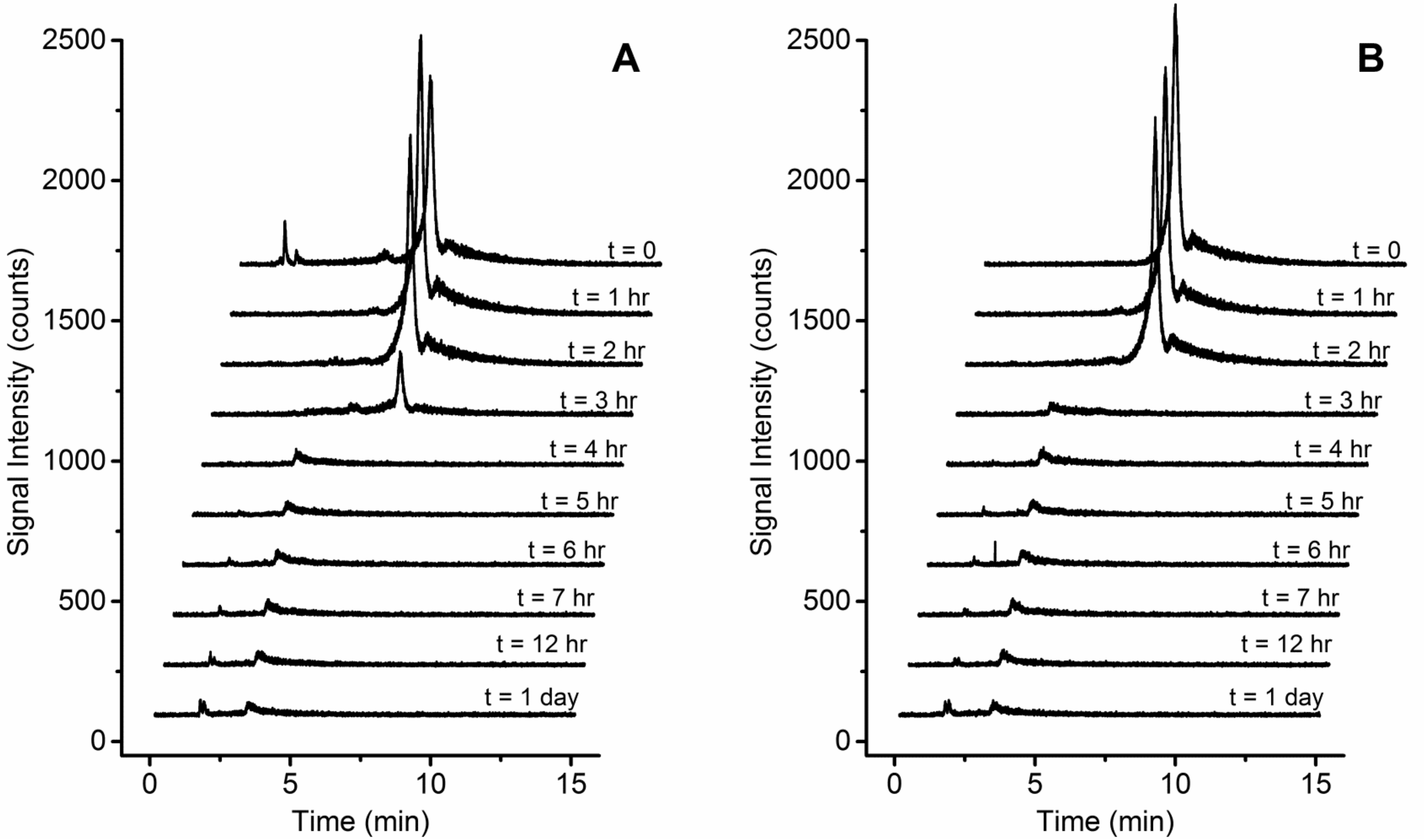

**Figure 4-5** **Effect of permanganate on the speciation of Au(I)-thiosulfate.**

*Chromatograms show the Au(I)-thiosulfate peak intensity greatly decreased after 2 hours, and the Au(III) peak increasing after 4 hours, under (A) air and (B) argon; Other conditions as Figure 4-1.*

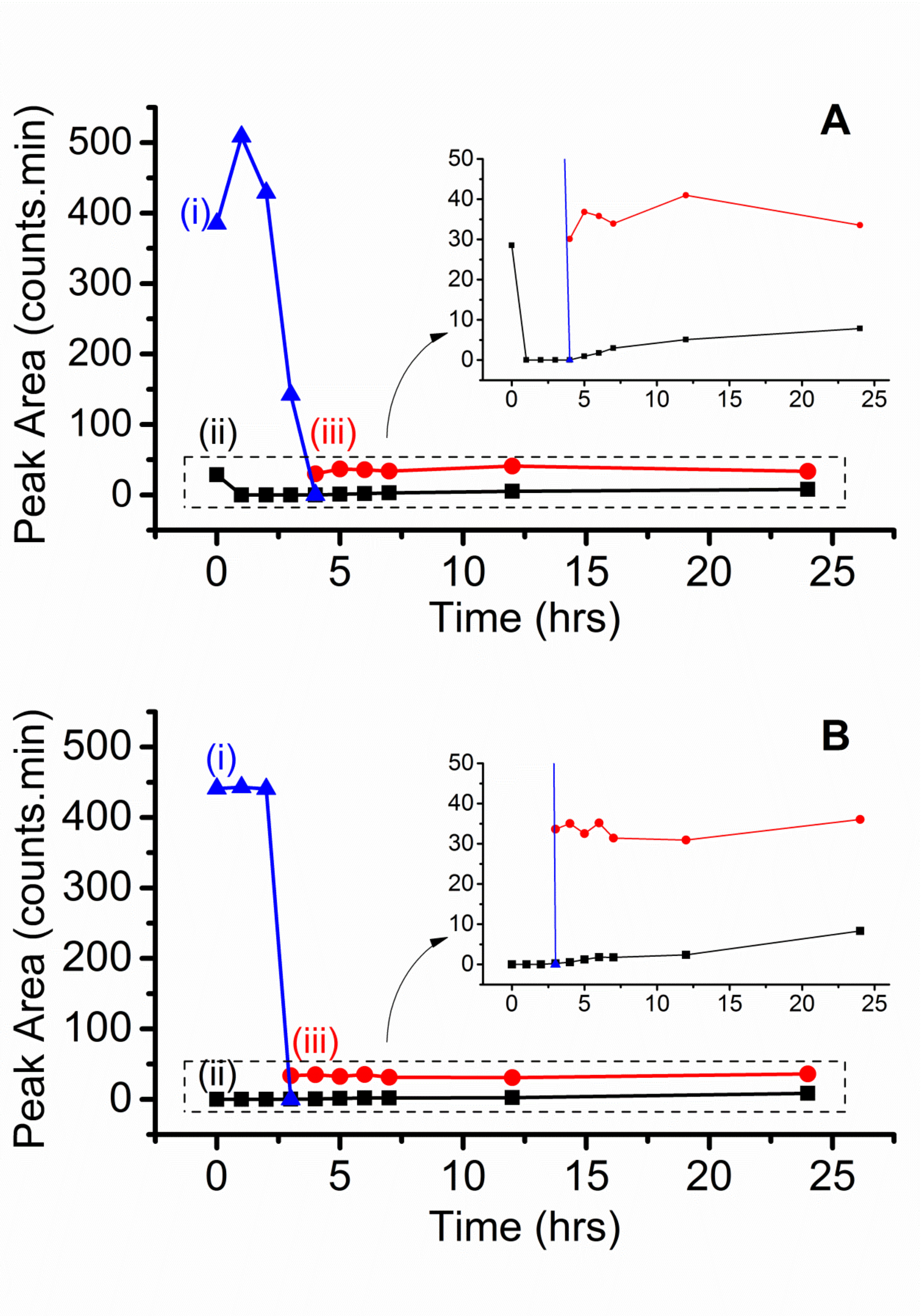

**Figure 4-6** **Effect of permanganate on the speciation of Au(I)-thiosulfate over 24 hours.**

*Plots show the peak areas (from Figure 4-5) of (i) Au(I)-thiosulfate, (ii) Au(III)-complexes and (iii) the unknown steady state complex over 24 hours; under (A) air and (B) argon.*

The oxidation of Au(I)-thiosulfate by $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ under both atmospheric and deoxygentated conditions are shown in Figure 4-7. Similar to the above $KMnO_4$ reaction, the Au(I)-thiosulfate is removed from solution rapidly, while the production of the Au(III) occurs at a much slower rate. It can be seen that there is more than one Au(III) complex at the beginning, however, there is only a single complex at t = 24 hours. Figure 4-8 shows there is an increase in the rate of Au(III) produced after the removal of Au(I)-thiosulfate from solution (t = 4 hrs). These observations suggest that 1) the Au(I)-thiosulfate is sorbed onto a manganese solid and 2) the Au(III) complexes formed within the first few hours are different to the those present at the end of the 24 hours. The mechanism for the oxidation of Au(I) to Au(III) by the $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ complex is likely to be similar to the $KMnO_4$ mechanism described above, as $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ is a heterogeneous catalyst (its amount exceeds its solubility in water) and therefore, provides a surface for the initial adsorption of Au(I) ions [227, 232].

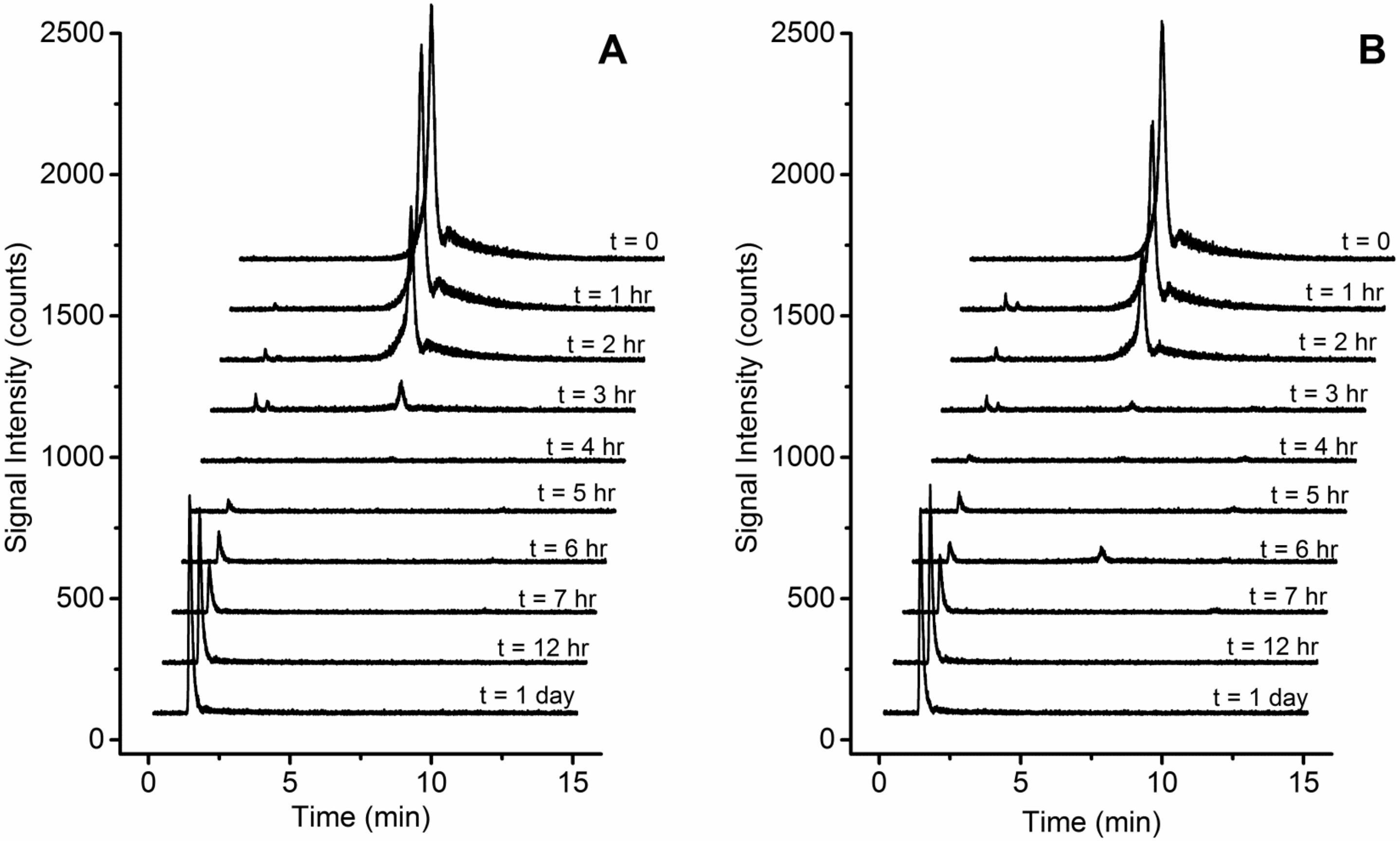

**Figure 4-7** **Effect of $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ on the speciation of Au(I) thiosulfate.**

*Chromatograms show the Au(I)-thiosulfate peak intensity has greatly decreased after 3 hours, and the Au(III) chloride peak intensity increasing after an hour, under (A) air and (B) argon. Other conditions as Figure 4-1.*

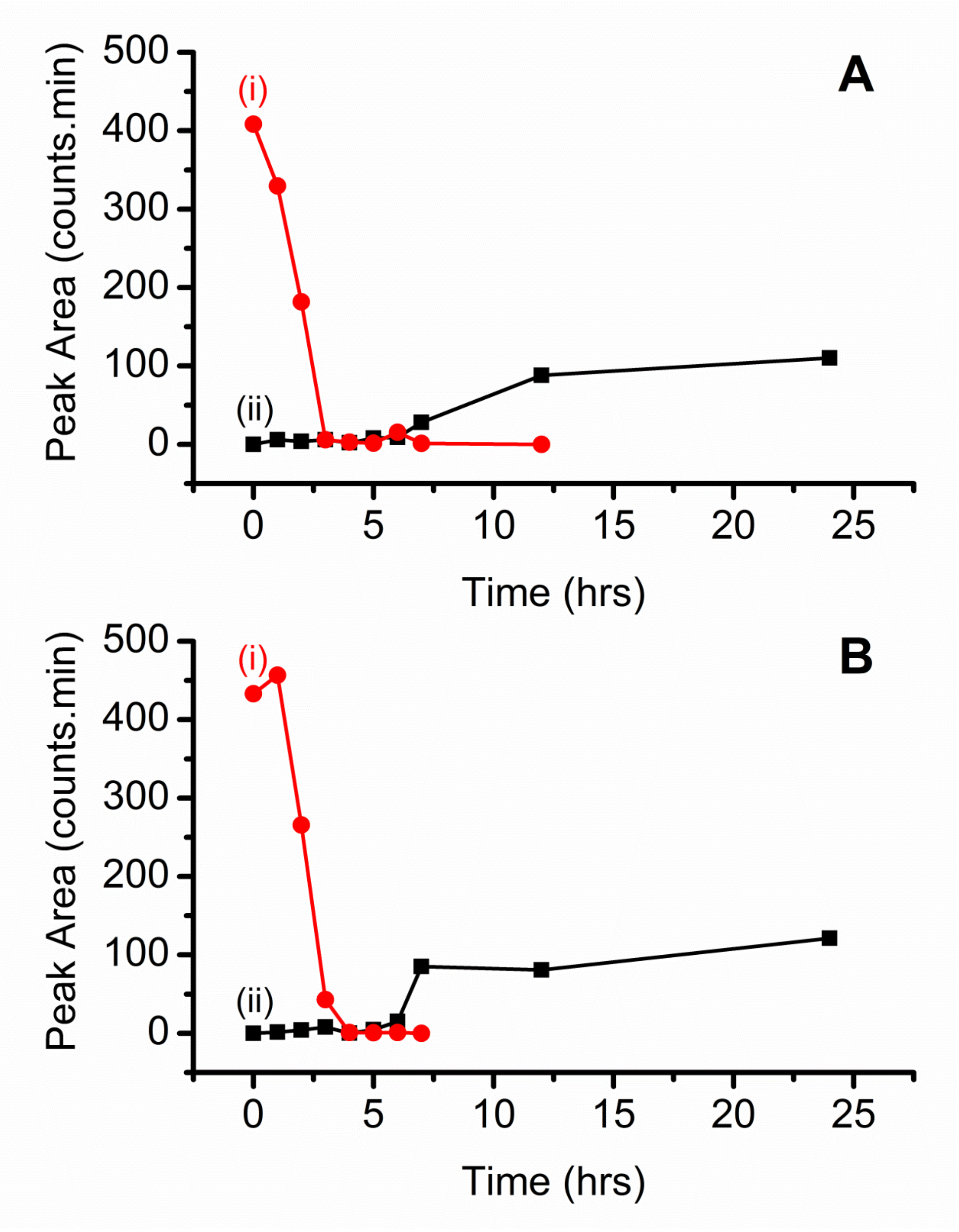

**Figure 4-8** **Effect of [(bpy)$_2$Mn$^{III}$(μ-O)$_2$Mn$^{IV}$(bpy)$_2$]$^{3-}$ on Au(I)-thiosulfate over time.**

*Plots show the peak areas for (i) Au(I)-thiosulfate and the increase for the (ii) Au(III)-complexes under (A) air and (B) argon from Figure 4-7.*

### 4.4.4 Kinetics of Au(0) Oxidation with $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$

While potassium permanganate was only able to slightly dissolve Au(0) into solution, as shown in Figure 4-4, a clear Au(III) peak is present with the $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ reaction after one day. The oxidation of Au(0) to Au(III) by $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ was monitored over 24 hours to determine whether an intermediate Au(I)-complex formed within this period (Figure 4-9). The resultant peak areas from the oxidation reactions under (A) air and (B) argon are plotted in Figure 4-10.

Interestingly, the level of Au(III) from the argon reaction plateaus after five hours Figure 4-10 (B) whilst the reaction under air Figure 4-10 (A) continues to increase over time. This indicates that oxygen plays a role in the reaction mechanism. The observed reaction under argon may be due to small amounts of $O_2$ dissolved in solution from the oxidation of water by $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ [228-230].

$$2H_2O \overset{hv}{\rightarrow} O_2+4H^{+}+4e^{-}$$

Whilst this oxidation of water is photocatalysed, and the reaction was kept in the dark, it may have been activated during the preparation steps which were undertaken under ambient light (i.e. weighing the $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$, sparging the argon reaction, and adding the reactants together etc.). Therefore, the oxidation in the initial five hours of the argon reaction may be driven by the production of oxygen by the $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ complex during the reagent preparation. The plateau after t = 5 hours, could be due to the consumption of the $O_2$. Further tests would be required to assess this theory.

Additionally, both reactions show the presence of very small quantities of Au(I), although it is unclear whether this is an intermediate product. It is possible that the production of Au(III) occurs via a multistep process whereby Au(0) is oxidised to Au(I) prior to the oxidation of Au(I) to Au(III). The very low levels indicate that the Au(I) is either rapidly oxidised or adsorbed onto a surface. The adsorption onto a surface would be consistent with the oxidation of Au(I) to Au(III) observed earlier.

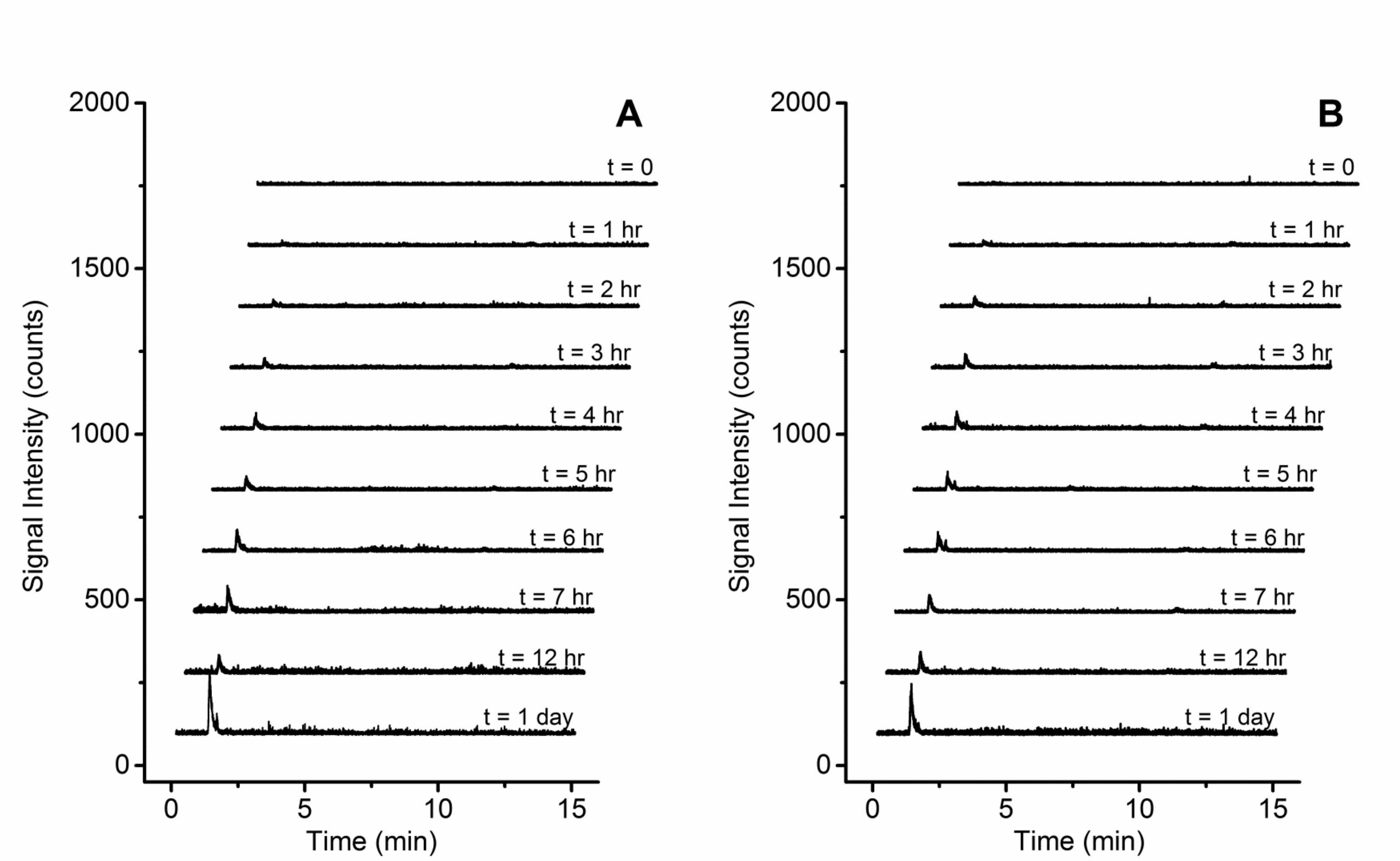

**Figure 4-9** **Effect of $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ on the speciation of Au(0).**

*Chromatograms show the Au(III) peak forming after one hour under (A) air and (B) argon. Other conditions as Figure 4-1.*

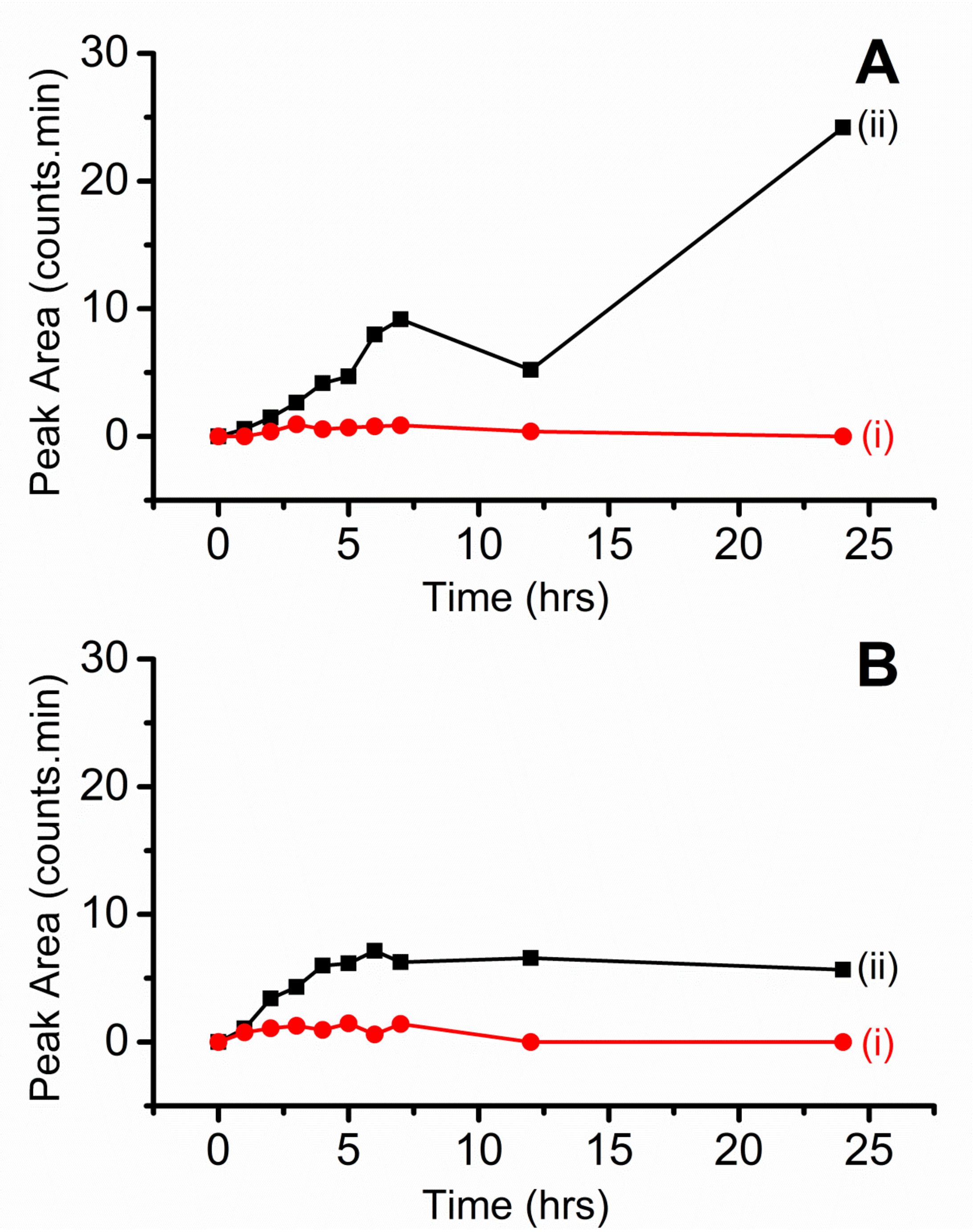

**Figure 4-10** **Effect of $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ on the speciation of Au(0) over time.** *Plots show the changes in peak area for (i) the Au(I)-complex and (ii) the Au(III)-complex; under (A) air and (B) argon from Figure 4-9.*

### 4.4.5 Implications for the mobility of gold

Presented in this chapter, are original experiments showing the oxidation of Au(I) to Au(III) by both $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ and potassium permanganate and Au(0) to Au(III) by $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$. Our studies indicate that under the conditions studied (0.01 M $Cl^-$ and ~0.0001 M Mn-compound), the formation of aqueous Au(III) from either Au(I)-thiosulfate or Au(0) powder:

1) requires a powerful oxidant,
2) occurs via a multistep process – where both aqueous and colloidal Mn are present in the system, and
3) can occur under both oxic and anoxic conditions.

Specifically, the oxidation of Au(0) to Au(III) is influenced by oxygen, while the oxidation of Au(I)-thiosulfate to Au(III), appears to occur through a different mechanism, where oxidation:

1) mainly occurs after the removal of Au(I)-thiosulfate from solution,
2) may be driven by the formation of a manganese solid and the subsequent adsorption of Au(I)-thiosulfate onto the surface, and
3) produces different Au(III) complexes depending on which manganese oxidant is used, suggesting that Au(III)-Mn complexes may be formed.

Our findings for the oxidation of Au(I) by permanganate support previous studies in the permanganate oxidation of As(III), where the production of a Mn-solid product, followed by the sorption of As(III) on to the Mn-solid and oxidation of As(III) was reported [222, 223]. This formation of a solid would result in less contact between the manganese and Au(0) powder, thus, explaining why so little solubilisation was observed in that reaction.

The $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ oxidation mechanism is more complex, due to its ability to catalyse the oxidation of water [227]. Without further work, it is uncertain how much of the Au(III) formation is from direct reaction with the $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ surface, or from the oxygen and hydrogen ions evolved from the splitting of water (It is possible that the oxidation of Au(I) is driven from the former and the oxidation of Au(III) from the latter). Further studies are also required in order to identify the intermediate and final products of the oxidation process (i.e. manganese speciation analysis, XRD analysis of any intermediate products, using gold leaf instead of gold powder and observing the reaction with microscopy).

The reactivity of gold with $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$, a biomimetic complex of those in enzymes involved in the photosynthesis of water, suggests that biogenic analogues in the environment may also be able to oxidise gold, however, future studies with such biogenic oxomanganese complexes are required. Other binuclear manganese complexes of biological significance (involved with the removal of hydrogen peroxide (protection of living cells against oxidative stress) and the reduction of ribonucleotides) may also be worth investigating [203-206]. Future work could also explore the effect of the biogenic formation of Mn(III/IV) oxides on gold, as Mn(II) oxidising bacteria (such as *Leptothrix discophora* SS1) may also catalyse the oxidation of Co(II) [208].

In regards to the Lake Way water, the detection of aqueous Au(III) in that near neutral water remains unexplained. Whilst the formation of aqueous oxidation products (such as As(III)→As(V) and Cr(III)→C(VI) by manganese oxides has been observed at neutral and alkaline conditions [175, 177], the formation of aqueous Au(III) from Au(I) was not observed with natural or synthetic manganese minerals under circumneutral to alkaline conditions.

For the oxidation of gold by manganese oxides, Boyle [1] and Emmons [2] suggested that acidic conditions were necessary to dissolve chloride minerals to provide free chlorine for the formation of aqueous gold complexes (i.e. $[AuCl_4]^-$). Whilst dissolved chloride was present in all our experiments, the waters tested were not very acidic (pH 4 - circum neutral) and may not be sufficient for the production of free chlorine. Therefore, we hypothesise that more acidic conditions are necessary to promote the reduction of manganese oxides. In addition to Au(I) adsorption onto the surface, the reduction or disproportionation of the manganese oxide (as shown by the permanganate reaction) appears to be necessary for the formation of aqueous Au(III) [176]. This work supports previous hypotheses that gold is only mobilised by manganese (as an aqueous complex) in acidic environments (which aids the reduction of manganese oxides), or when bound to colloidal manganese in neutral to alkaline waters [1, 2].

## 4.5 Conclusions

Although thermodynamic modelling predicts Au(I) species to be most stable, the speciation analysis of water from the Lake Way water, revealed the presence of Au(III) species. The presence of manganese in those waters, (along with previous studies that have shown the oxidation of gold and other metal ions by manganese oxides), suggests that the Au(III) species detected may arise from oxidation by manganese compounds.

Various manganese oxides (synthetic and natural samples) were stirred over time with either Au(I)-thiosulfate, or Au(0) powder, in the presence of sodium chloride. Any changes to the speciation of gold were monitored with the HPLC-ICP-MS method developed in Chapter 2. The formation of aqueous Au(III) from Au(I) was not observed with manganese minerals under circumneutral to alkaline conditions, however, oxidation was observed in the permanganate reaction. This suggests that the oxidation of gold relies on the ability of the manganese oxides to reduce/disproportionate. In the environment, the reduction of manganese oxides occurs mainly in acidic conditions, therefore, the presence of Au(III) in the Lake way waters remains unexplained.

The oxidation of both Au(0) and Au(I)-thiosulfate to Au(III) by synthetic $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)2]^{3-}$ was also demonstrated in the absence and presence of atmospheric oxygen. Thus the oxidation of gold by bacterially produced oxomanganese complexes, similar to $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)2]^{3-}$, may be responsible for Au(III) complexes in groundwaters and should be explored in future work. The study of this biomimetic compound and its role in gold oxidation may also be important for the dissolution of metallic gold and could present an alternative to common lixiviants used in the refinement and leaching of gold in mining processes.