The Speciation of Gold in Mine Wastes and Natural Waters

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5. Conclusions and Future Work

5.1 Conclusions

Prior to this work, the use of HPLC-ICP-MS for the speciation of gold was limited to the detection of gold-based drugs and their metabolites in biological fluids. Chapter 2 describes the first development of a HPLC-ICP-MS method for the determination of Au(I)-cyanide, Au(I)-thiosulfate, Au(III)-chloro-hydroxyl and Au(III)-bromo-hydroxyl complexes in mine waters and groundwaters with HPLC-ICP-MS. The detection limits for these species were 0.21 μg L^{-1}, 0.58 μg L^{-1}, 0.081 μg L^{-1} and 0.17 μg L^{-1} respectively.

Sixty two water samples (from mining processes, groundwaters and environmental monitoring bores) were collected from around Australia and analysed with the developed method. Chapter 3 describes the detection of Au(I)-cyanide and Au(III)-complexes in mine waters and groundwater by HPLC-ICP-MS. Trace amounts of Au(I)-cyanide were determined in a few environmental monitoring bores, of which the proximity to tailings dams and other mining processes suggests that the Au(I)-cyanide arose from leached mining processes. Unexpectedly, Au(III) was detected in a near-neutral, saline groundwater, even though Au(III) is predicted to be thermodynamically unstable at those conditions. 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 order to identify the Au(III) complex detected, the chemical composition of the Lake Way water and other saline water samples were investigated. The apparent correlation of manganese with Au(III), led to an investigation into the effect of manganese on the speciation of gold in Chapter 4.

Various manganese compounds (including natural manganese minerals and synthetic manganese compounds) were tested for their ability to either oxidise Au(I)-thiosulfate or Au(0) to aqueous Au(III), under conditions similar to the Lake Way sample. The detection of Au(III) in the Lake Way sample remains unexplained, as the formation of aqueous Au(III) was not observed with the natural manganese oxides (or the synthetic minerals), the forms of manganese most likely to exist around the Lake Way waters.

Both potassium permanganate and $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ complex were also tested and found to be able to oxidise Au(I) and Au(0) to form Au(III), under oxic and anoxic conditions. The oxidation mechanisms for Au(I) and Au(0) appear to be different: the production of Au(III) from Au(I) occur primarily after the removal of Au(I) from solution, while the Au(0) reaction appears to be influence by oxygen. The fact that the removal of Au(I) from solution precedes the formation of Au(III), implies that the potassium permanganate and $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ complex may transform into a colloidal form that adsorbs the

Au(I). We propose that the presence of O_2 is necessary for the oxidation of Au(0) to Au(I), and the reduction or disproportionation of the manganese oxide followed by the adsorption of Au(I) appears to be necessary for the oxidation of Au(I) to Au(III).

5.2 Future work

5.2.1 Groundwater analysis

Direct measurements of Au speciation in groundwater by HPLC-ICP-MS allows for example to distinguish uncontaminated from contaminated (cyanide) aquifers. The method also provides a direct insight about the process of Au transport. This information is critical in evaluating results for hydrogeochemical exploration surveys. However, the future studies mentioned below are necessary to further advance the use of groundwater for the mineral exploration of gold.

The detection limits for Au(I)-thiosulfate was slightly higher than the other gold standards due to the partial formation of Au(I)-cyanide (when [Au] < 1 $\mu g\ L^{-1}$) from cyanide impurities in the mobile phase. The detection limit may be improved by purifying the acetonitrile to remove cyanide, although acetonitrile also contain trace amounts of methyl cyanides that may also complex to gold. Changing the LC column to a narrower-bore column may also improved the detection limits of the method. A lot of groundwaters are quite saline and therefore the effect of dissolved salts on the speciation methods (e.g. matrix peaks) should be further investigated.

Improving the sample storage procedure is a key requirement for further work. HPLC-ICP-MS analysis of many waters did not detect any gold, although gold was detected by ICP-MS (e.g., Sunlight Gold Mine, Oberon, British King, Darlot Batterie, Plutonic West 2, Wildara and the Fifield Bores). It is thought that this was due to adsorption onto the plastic container during storage. Future work should incorporate studies into the stability of gold species under long-term storage. Acid washing the storage bottles and the use of plastic over glass bottles have also been implied to increase the sorption effect of gold on storage bottles [94, 233]. Therefore future studies must examine the effects of prewashing the storage bottles, freezing samples, and using different types of storage containers and determine the optimal compromise between preservation of the sample and ease of transport.

Gold is also mobilised as gold nanoparticles and as gold organic complexes in the environment. Therefore other speciation methods for these species must be accounted for in further investigations.

5.2.2 Remediation and Recovery Processes

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 [94]. Although Au(I)-cyanide was detected in the Agnew and Granites environmental monitoring bores, chemical and speciation analysis of the tailings and the soil from around those monitoring bores may explain the formation and distribution of Au(I)-cyanide detected.

5.2.3 Manganese and Gold

Whilst monitoring the oxidation reactions provided some information on the mechanism of oxidation, further analyses need to be conducted to identify the Au(III) complexes and any intermediate products produced in the permanganate and $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ reactions. Monitoring the speciation of manganese may confirm the whether any manganese bound Au(I) or Au(III) complexes are produced. Filtering the reaction solutions and analysing collected particles with surface analysis techniques (scanning electron microscopy, x-ray absorption spectroscopy or x-ray diffraction) will confirm our hypotheses that Au(I) oxidation occurs on the surface of a manganese solid and identify the manganese solid produced in the reactions.

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). Monitoring the levels of dissolved oxygen during the reaction and/or bubbling oxygen into the system will provide more information about the effects of oxygen on the oxidation of gold. Replacing gold powder with gold leaf will also allow the reaction to be observed on the gold surface with microscopy techniques.

Other biogenic complexes, similar to $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ may also be able to mobilise gold in the environment. 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].

Whilst the formation of aqueous Au(III) was not observed with the natural manganese minerals, the removal of Au(I)-thiosulfate from solution was. In order to determine if Au(I) was adsorbed onto the mineral surface and oxidised, surface analysis of the mineral particles (i.e. scanning electron microscopy or x-ray absorption spectroscopy) should be conducted. The reactions should also be acidified and the solutions reanalysed to see whether Au(III) formed on the mineral surface could be washed into solution. Previous gold dissolution experiments conducted by Rickard [181] and Cloke and Kelly [180] should be

In addition to Mn(IV), Goldschmidt [179] suggested that Fe(III) ions may be responsible for the solubilisation of gold in the weathering environment (goethite has also been shown to slightly solubilise gold [180]). As the chemistry of manganese and iron are closely linked in the environment, conducting a similar study with iron oxides may improve our understanding of the mobilisation of gold in the environment.

Although the detection of Au(III) in the Lake Way water remains unexplained, further analysis on the Lake Way sediment and investigating the microbiota that live in these soils may also provide more information on how Au(III) was formed in these waters at near-neutral pH.

5.2.4 Thermodynamic models

Now that we have shown that HPLC-ICP-MS is capable of measuring different gold complexes, this method should be applied to the previous experiments that form the basis for the thermodynamic models used to understand how gold exists in the environment. Although adjusting the method (or expanding the method to include different gold complexes) may be necessary, previous studies should be revisited, including:

1. The Au(I)-chloro-hydroxyl system has been calculated by gold solubility experiments [72] and derived from experiments conducted at hydrothermal conditions (>100 ºC), where such complexes are most stable and have not been measured at surface temperatures [82, 190].
2. The Au(I)-sulfur system (including the bisulfide and hydroxyl ligands) theoretically calculated by Tossell [71] with quantum chemistry.
3. The Au(III)-chloro-hydroxyl system has been extensively studied with Raman and UV-VIS [81-84], however, comparison between the various studies is difficult due to the different experimental conditions in the studies.
4. The Au-humic acid system where it is unclear whether humic acids assist the dissolution of gold [40, 234-236] or causes reduction to form gold colloids [36, 42-44].