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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Declaration

'I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text’.

Christine Ta

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Summary

The geomicrobiological cycle of gold has been widely studied in an effort to improve gold exploration techniques and gold recovery in mining processes. But these studies and the basic understanding of how aqueous gold behaves are largely based on chemical speciation modelling (indirect speciation), as current direct speciation techniques are limited by their poor sensitivity and interferences from real matrices.

This study describes the 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. A systematic study of the HPLC variables led to the final mobile phase: a buffer of 1 mM tetrabutylammonium chloride and 5 mM sodium dihydrogen phosphate/disodium hydrogen phosphate prepared in 6: 17.5: 76.5 v/v/v isopropanol: acetonitrile: water. The detection limits for the gold species ranged from 0.081-0.58 $\mu g\ L^{-1}$.

Sixty two water samples (from mine waters, groundwaters and environmental monitoring bores) were collected from around Australia and analysed with the developed method. Trace amounts of Au(I)-cyanide were detected in a few environmental monitoring bores (~0.7 – 11 $\mu g\ L^{-1}$), 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 (~0.4 $\mu g\ L^{-1}$), even though Au(III) is predicted to be thermodynamically unstable at those conditions. Chemical analysis of saline groundwater samples revealed an apparent correlation between manganese and Au(III) and led to an investigation into the effect of manganese on the speciation of gold.

Preliminary studies investigating the ability of various natural 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 (similar to the saline groundwaters collected). Synthetic analogues of manganese oxides (including pyrolusite and potassium

permanganate) were also tested. These reactions comprised of stirring ~0.0001 M Mn-oxide and 0.1 M Cl^- with either Au(I)-thiosulfate ([Au] = 1 mg L^{-1}) or Au(0) powder ([Au] = 50 mg L^{-1}) made up to 100 mL with water.

The formation of aqueous Au(III) from Au(I) was not observed with natural or synthetic manganese minerals under circumneutral to alkaline conditions, but was observed for permanganate (at pH 6.9) and $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3-}$ (pH 4.7). Both compounds were also observed to oxidise Au(0) powder to aqueous Au(III). These preliminary studies support previous hypotheses by Boyle [1] and Emmons [2] that gold can be mobilised by manganese in the environment, and may have provided further details on the mechanism for the mobilisation of gold by manganese in the environment. 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).

In summary, due to the limited techniques able to directly speciate gold at environmentally relevant concentrations, the development of a sensitive and direct speciation method to enhance current understanding of the geomicrobiological cycle of gold is required. The research presented here may advance the use of HPLC-ICP-MS as a technique for mineral exploration, in studies on the fate of gold in mine wastes and bioremediation processes, and in studies on the effect of organic matter, microorganisms and minerals on the speciation of gold.

Dedicated to

My Parents
Kuan and Mayling Ta

Contents

Figures

Tables

List Of Acronyms

AAS	Atomic Absorption Spectroscopy
APHA	American Public Health Association
bpy	2,2'-bipyridyl
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DC	Dissolved Carbon
DOC	Dissolved Organic Carbon
EC	Electrical Conductivity
EXAFS	Extended X-ray Absorption Fine Structure
GNP	Gold Nanoparticle
GWB	The Geochemist's Workbench®
HA	Humic Acid
HDTMAOH	Hexadecyltrimethylammonium Hydroxide
HPLC	High Performance Liquid Chromatography
IC	Inorganic Carbon
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
ID	Internal Diameter
LMCT	Ligand-to-Metal Charge Transfer
LOD	Limit of Detection
LOQ	Limit of Quantitation
m/z	Mass-to-Charge Ratio
PIRSA	Department of Primary Industries and Resources of South Australia
PVDF	Polyvinylidene Difluoride
QPC	Quartz Pebble Conglomerate
RP-IPC	Reversed Phase-Ion Pairing Chromatography
RR	Resonance Raman
TACN	Triazacyclononane
TBAC	Tetrabutylammonium Chloride
TBAOH	Tetrabutylammonium Hydroxide
TEAOH	Tetraethylammonium Hydroxide
TN	Total Nitrogen
TPAOH	Tetrapropylammonium Hydroxide
UV-VIS	Ultraviolet-Visible

XANES	X-ray Absorption Near Edge Structure
XAS	X-ray Absorption Spectroscopy
XRD	X-ray Diffraction