# THE SORPTION OF GOLD AND SILVER ON SOIL MINERALS

*D.J. Gray*

**CRC LEME OPEN FILE REPORT 42**

**September 1998**

(CSIRO Division of Exploration Geoscience Report 127R, 1990.
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# RESEARCH ARISING FROM CSIRO/AMIRA REGOLITH GEOCHEMISTRY PROJECTS 1987-1993

In 1987, CSIRO commenced a series of multi-client research projects in regolith geology and geochemistry which were sponsored by companies in the Australian mining industry, through the Australian Mineral Industries Research Association Limited (AMIRA). The initial research program, "Exploration for concealed gold deposits, Yilgarn Block, Western Australia" (1987-1993) had the aim of developing improved geological, geochemical and geophysical methods for mineral exploration that would facilitate the location of blind, buried or deeply weathered gold deposits. The program included the following projects:

**P240: Laterite geochemistry for detecting concealed mineral deposits (1987-1991).** Leader: Dr R.E. Smith.
Its scope was development of methods for sampling and interpretation of multi-element laterite geochemistry data and application of multi-element techniques to gold and polymetallic mineral exploration in weathered terrain. The project emphasised viewing laterite geochemical dispersion patterns in their regolith-landform context at local and district scales. It was supported by 30 companies.

**P241: Gold and associated elements in the regolith - dispersion processes and implications for exploration (1987-1991).** Leader: Dr C.R.M. Butt.
The project investigated the distribution of ore and indicator elements in the regolith. It included studies of the mineralogical and geochemical characteristics of weathered ore deposits and wall rocks, and the chemical controls on element dispersion and concentration during regolith evolution. This was to increase the effectiveness of geochemical exploration in weathered terrain through improved understanding of weathering processes. It was supported by 26 companies.

These projects represented "an opportunity for the mineral industry to participate in a multi-disciplinary program of geoscience research aimed at developing new geological, geochemical and geophysical methods for exploration in deeply weathered Archaean terrains". This initiative recognised the unique opportunities, created by exploration and open-cut mining, to conduct detailed studies of the weathered zone, with particular emphasis on the near-surface expression of gold mineralisation. The skills of existing and specially recruited research staff from the Floreat Park and North Ryde laboratories (of the then Divisions of Minerals and Geochemistry, and Mineral Physics and Mineralogy, subsequently Exploration Geoscience and later Exploration and Mining) were integrated to form a task force with expertise in geology, mineralogy, geochemistry and geophysics. Several staff participated in more than one project. Following completion of the original projects, two continuation projects were developed.

**P240A: Geochemical exploration in complex lateritic environments of the Yilgarn Craton, Western Australia (1991-1993).** Leaders: Drs R.E. Smith and R.R. Anand.
The approach of viewing geochemical dispersion within a well-controlled and well-understood regolith-landform and bedrock framework at detailed and district scales continued. In this extension, focus was particularly on areas of transported cover and on more complex lateritic environments typified by the Kalgoorlie regional study. This was supported by 17 companies.

**P241A: Gold and associated elements in the regolith - dispersion processes and implications for exploration.** Leader: Dr. C.R.M. Butt.
The significance of gold mobilisation under present-day conditions, particularly the important relationship with pedogenic carbonate, was investigated further. In addition, attention was focussed on the recognition of primary lithologies from their weathered equivalents. This project was supported by 14 companies.

Although the confidentiality periods of the research reports have expired, the last in December 1994, they have not been made public until now. Publishing the reports through the CRC LEME Report Series is seen as an appropriate means of doing this. By making available the results of the research and the authors' interpretations, it is hoped that the reports will provide source data for future research and be useful for teaching. CRC LEME acknowledges the Australian Mineral Industries Research Association and CSIRO Division of Exploration and Mining for authorisation to publish these reports. It is intended that publication of the reports will be a substantial additional factor in transferring technology to aid the Australian Mineral Industry.

# PREFACE

This preliminary investigation of the sorption of Au and Ag complexes is a study of an important but poorly understood area of Au geochemistry - the mechanisms whereby Au is immobilized, and how this is related to solution conditions and the solid matrix of the soil with which it interacts. Understanding this subject is important for our understanding of the mechanisms of soil Au anomaly formation and deciding how to most effectively use soil as an exploration medium. Specifically, the study:

    (i)   demonstrates the poor solubility of Au and Ag in a humate solution;

    (ii)   shows that the Au and Ag thiosulphates are soluble in a number of differing environments, but the Au and Ag are readily precipitated by Mn oxides;

    (iii)   demonstrates the greater mobility of Ag than Au in acid/saline environments;

    (iv)   suggests that Au complexed by chloride or iodide is soluble only in the presence of Mn oxides, in contrast to the effect of Mn oxides on thiosulphate complexes of Au and Ag;

    (v)   demonstrates the ability of, as yet undetermined, but possibly biologically generated, species released by soils to mobilize Au.

This investigation is complementary to other investigations of Au chemistry and studies of the nature and surface expression of gold mineralization. Together they address many of the principal objectives of the Project.

C.R.M. Butt,
Project Leader.
November, 1990

# ABSTRACT

The sorption of Au and Ag was investigated by reacting synthesized Au and Ag complexes with a range of different soils. The systems used were Au and Ag in humic, thiosulphate, iodide and chloride solutions, and in a poorly complexed form.

Soils used were 4% Peat Moss / 96% Quartz, organic rich soil sample 1467, Fe oxide rich soil sample 1468, carbonate rich soil sample 1470, Fe oxide rich standard 7, Mn oxide rich Mount Keith Shaft, 44 m depth, and a Mn oxide rich segregation collected at Ora Banda.

The solutions and soils were equilibrated together and the Au and Ag concentrations in the soil solutions were measured at two weeks and again at three months.

Gold and Ag thiosulphates had a high initial solubility when contacting most of the soils, with the exception of the Mn rich soils, which quickly sorbed most of the Au and Ag. In general, both Au and Ag had similar solubilities in thiosulphate solution. When finally sorbed, Au did not redissolve.

In an acidic chloride-rich solution Au was more readily sorbed than Ag, only having an appreciable solubility when in contact with the most Mn rich material. This contrasts with the results for thiosulphate complexes, demonstrating the critical importance of the Au complex on the extent of sorption. Results were similar for Au iodide.

Humate complexes were found to maintain only small concentrations of Au in solution, suggesting a weak interaction between Au and humate. This is in contrast with work on Au humate interactions by other workers which has suggested that humate can be very effective at dissolving Au.

An important observation is the ability of the soils to redissolve Au. When the uncomplexed Au and Ag were mixed with the various soils they were quickly sorbed. After three months, however, a number of the mixtures contained significant quantities of dissolved Au (but not Ag). This is possibly due to soluble species with a high affinity for Au being produced by biological activity. Very similar effects were also observed for Au iodide. The humate mixtures also showed appreciable redissolution of Au, though in a different manner to the uncomplexed and the iodide mixtures, possibly due to the different types and concentrations of organic matter in the humate mixtures. These results suggest that Au is readily mobilized in soils, and this metal should be considered to be mobile under such environments.

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# LIST OF ABBREVIATIONS

mM      millimoles/litre
M       moles/litre
OC      Organic Carbon

# 1. Introduction

The chemical re-distribution of Au in soils is controlled by physico-chemical factors that determine the nature of the processes that may cause mobilization and precipitation. Mobilization is initiated by dissolution of the primary Au, by the processes discussed by Gray (1988). Subsequent groundwater investigations have indicated mobilization of Au by thiosulphate (Gray, 1990a), or by the halide ligands Cl⁻ and I⁻ (Gray, 1990b) at different sites within Western Australia. Soil studies (Gray *et al.*, 1990a) have shown that Au is mobilized in soils by as yet undetermined, probably organic, ligands, possibly supplemented by bacterial activity. A number of investigations (Friese, 1931; Baker, 1973, 1978; Boyle *et al.*, 1975; Gray *et al.*, 1990b) have also suggested Au mobilization as a humate complex.

Each of these Au complexes is formed by different processes (Gray, 1988). The processes leading to the immobilization of Au, and how they are influenced by factors such as the Au complex, water chemistry and soil mineralogy are less well understood. This report is a preliminary investigation into the inter-relationships of these factors, and how they affect the mobilization of Au and Ag. The particular species studied were the thiosulphate, humate and chloride complexes of Au and Ag, and the iodide complex of Au. Soil samples [1] included organic-, carbonate-, Fe oxide- and Mn oxide-rich samples. The experimental conditions were designed to study as many feasible water-soil interactions as possible.

This report describes the initial study of the sorption [2] of Au and Ag onto different soil materials, where the Au and Ag are initially present in a number of different forms. Results indicate the critical effect of both the form of the Au and Ag, and the soil material with which it is interacting, on the mobility of these metals.

# 2. Materials and Methods

## 2.1. Soil Materials

Seven soil types were selected. These were:

(i)   Peat moss:  4% commercially purchased Yates Peat Moss mixed with 96% crushed quartz;
(ii)  1467:  organic rich soil sample 1467;
(iii) 1468:  Fe oxide rich soil sample 1468;
(iv)  1470:  carbonate rich soil sample 1470;
(v)   Std. 7:  Fe oxide rich standard 7;
(vi)  Mount Keith (MKD):  Mn oxide rich Mount Keith Shaft 44 m saprolite;

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[1] Note that, for simplicity, the term soil is used in this report to include the Mn oxide-rich saprolites from Mt. Keith and Siberia.

[2] The terms "sorption" and "sorbed" are used as umbrella terms to describe all reactions that may remove Au and Ag from solution. This could include adsorption, precipitation, decomposition of the ligand by agents released from the soil, or bacterial uptake of Au and Ag, amongst others.

(vii) Ora Banda (OB): Mn oxide rich segregation, Siberia.

Samples 1467, 1468 and 1470 were taken from a Au rich profile within the Bounty Pit, at Mt. Hope, while Std. 7 is from surface scrapings near Holleton. The chemistry and biogeochemistry of these samples have been studied extensively (Gray *et al.*, 1990a). The elemental compositions and the mineralogies of all of the samples are given in Tables 1 and 2.

## 2.2. Synthesis of Au/Ag Complexes

Solutions were made up, prior to addition to the soils, so as to contain approximately 10 mg/L Au and Ag, complexed with a particular ligand. Four different solutions were synthesized:

### 2.2.1. Humic Complex.

1.25 g of Aldrich Humic Acid, sodium salt, tech. (cat. no. H1,675-2 [3]) were added to approximately 100 mL deionized water, then Au and Ag standards were added so as to give a concentration of 10 mg/L when made up to final volume. The solution pH was maintained above 6 by addition of sodium hydroxide (NaOH) solution. The solution was made up to 250 mL final volume, stored in glass in the dark, and passed every three days through 0.45 µm millipore until there was no solid residue. The final solution was expected to contain 5000 mg/L humate (the humic acid being converted to humate at neutral pH) and 10 mg/L Au and 10 mg/L Ag, less any metal precipitated. Actual measured concentrations were 3.4 mg/L Au and 2.55 mg/L Ag. On the completion of the filtering the solution had an Eh of 430 mV (*i.e.*, moderately oxidizing) and a pH of 6.7.

### 2.2.2. Thiosulphate Complex.

0.248 g $Na_2S_2O_3 \cdot 5H_2O$ (248 g molecular weight) was mixed with approximately 50 mL deionized water, with $N_2$ bubbling. The pH was raised to 10 with NaOH solution, then Au and Ag standards added to give a concentration of 10 mg/L when made up to final volume. As the addition of the Au and Ag will tend to lower the pH of the solution, and thus destabilize the thiosulphate, this was done dropwise, and interspersed with addition of NaOH solution so as to maintain neutral to alkaline conditions. Following this, another 0.248 g $Na_2S_2O_3 \cdot 5H_2O$ was added, the solution taken to pH 7, made up to 100 mL final volume, and stored in glass in the dark. The final solution was expected to contain 20 mmoles/L (m$\underline{M}$) $S_2O_3^{2-}$ (less any decomposition) and 10 mg/L Au and 10 mg/L Ag (less any metal precipitated). Actual measured concentrations were 9.55 mg/L Au and 8.8 mg/L Ag.

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[3] Properties of this material are detailed in MacCarthy and Malcolm (1987).

Table 1: Elemental Compositions of Samples.

| | Method | Sample | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Moss | 1467 | 1468 | 1470 | Std. 7 | MKD | OB |
| pH | | 6.52 | 8.21 | 8.83 | 9.51 | 6.39 | 7.50 | 6.33 |
| OC | Titration | 1.31 | 1.06 | 0.69 | 0.26 | 1.22 | <0.05 | <0.05 |
| $SiO_2$ | ICP | 97.32 | 71.99 | 57.72 | 35.59 | 47.69 | 61.77 | 40.64 |
| $Al_2O_3$ | ICP | 0.12 | 13.70 | 15.85 | 13.59 | 18.44 | 0.42 | 4.23 |
| $Fe_2O_3$ | ICP | 0.84 | 9.95 | 17.69 | 15.80 | 31.56 | 18.23 | 27.43 |
| MgO | ICP | 0.05 | 1.43 | 2.26 | 12.63 | 0.23 | 0.55 | 1.50 |
| CaO | ICP | 0.26 | 0.72 | 4.41 | 20.49 | 0.24 | 0.23 | 0.13 |
| $Na_2O$ | XRF | 0 | 0.26 | 0.33 | 0.78 | 0.07 | 0.10 | 0.21 |
| $TiO_2$ | XRF | 0.04 | 0.64 | 0.73 | 0.56 | 1.67 | 0.03 | 1.32 |
| $P_2O_5$ | ICP | 0.05 | 0.03 | 0 | 0 | 0 | 0.05 | 0.12 |
| $SO_3$ | XRF | 0.04 | 0.03 | 0.04 | 0.14 | 0.07 | 0.03 | 0.17 |
| As | INAA | 0.7 | 16 | 35 | 37 | 76 | 86 | (21)* |
| Au | INAA | 0 | 1.01 | 3.56 | 6.07 | 0.67 | 0 | 0 |
| Ba | XRF | 20 | 113 | 193 | 214 | 42 | 31300 | 17300 |
| Be | ICP | 0.02 | 0 | 0.58 | 5.0 | 4.3 | 4.3 | 8.7 |
| Ce | INAA | 1.6 | 29 | 31 | 22 | 10 | 388 | 202 |
| Co | INAA | 0.7 | 27 | 27 | 22 | 11 | 33900 | 15400 |
| Cr | INAA | 6 | 640 | 1250 | 1200 | 465 | 550 | 4840 |
| Cu | XRF | 9 | 73 | 137 | 148 | 58 | 2840 | 267 |
| Ga | XRF | 1 | 18 | 25 | 23 | 39 | 0 | 16 |
| Ge | XRF | 0 | 1.12 | 0 | 0 | 1 | 4 | 3 |
| La | INAA | 1 | 17 | 18 | 14 | 6 | 197 | 132 |
| Mn | XRF | 46 | 539 | 589 | 479 | 207 | 25400 | 80100 |
| Mo | INAA | 1 | 4 | 5 | 6 | (2) | (66) | (48) |
| Nb | XRF | 0 | 6 | 8 | 4 | 9 | 0 | 2 |
| Ni | XRF | 8 | 180 | 202 | 148 | 49 | 49300 | 54500 |
| Pb | XRF | 0 | 11 | 19 | 13 | 26 | 0 | 7 |
| Rb | XRF | 0 | 40 | 36 | 26 | 14 | 1 | 8 |
| Sb | INAA | 0.2 | 0.6 | 1.9 | 0.6 | 1.2 | (3.5) | (2.4) |
| Sr | XRF | 6 | 54 | 127 | 824 | 15 | 120 | 2410 |
| V | XRF | 2 | 201 | 402 | 405 | 950 | 16 | 1100 |
| W | INAA | (0.2) | 3.5 | 4.5 | 4.7 | 13.6 | 308 | 203 |
| Y | XRF | 1.0 | 12.3 | 15.8 | 11.4 | 6.8 | 48 | 25 |
| Zn | XRF | 0 | 34 | 36 | 20 | 22 | 624 | 35 |
| Zr | XRF | 29 | 141 | 151 | 116 | 219 | 3 | 46 |

Corrected to dehydrated weight, all oxides and OC (organic carbon)in wt %, other elements in mg/kg.

nd:    not determined.
*:    Where value is in brackets, concentration is considered to be below the detection limit.

Table 2: Mineralogy of Samples

| Mineral phase | Formula | Moss | 1467 | 1468 | 1470 | Std. 7 | MKD | OB |
|---|---|---|---|---|---|---|---|---|
| Smectite | # | - | xxx | xxx | - | - | - | - |
| Kaolin | $Al_2Si_2O_5(OH)_4$ | - | xxx | xxx | xx | xxx | - | - |
| Quartz | $SiO_2$ | xxx | xxx | xx | x | xx | xxx | xx |
| Goethite | FeOOH | - | x | xx | x | x | - | - |
| Hematite | $Fe_2O_3$ | - | ? | ? | ? | xxx | xxx | xxx |
| Cryptomelane | $KMn_8O_{16}$ | - | - | - | - | - | - | xxx |
| Lithiophorite | (LiAlCoMn)OOH | - | - | - | - | - | xxx | xx |
| Anatase | $TiO_2$ | - | x | ? | - | - | - | - |
| Rutile | $TiO_2$ | - | x | ? | - | - | - | - |
| Calcite | $CaCO_3$ | - | - | xx | x | - | - | - |
| Dolomite | $MgCa(CO_3)_2$ | - | - | x | xxx | - | - | - |
| Feldspar | $(K,Na)AlSi_3O_8$ | - | - | - | x | - | - | - |

| # | Highly variable. A general formula is: $(^1/_2Ca,Na)_{0.35}(Al,Mg,Fe)_{2-3}[(Si,Al)_4O_{10}](OH)_2 \cdot nH_2O$. |
|---|---|
| xxx | major component |
| xx | minor component |
| x | trace component |
| ? | possible component |
| - | below detection |

### 2.2.3. Iodide Complex.

0.166 g KI (166 g molecular weight) was mixed with approximately 50 mL deionized water, and a Au standard added so as to give a concentration of 10 mg/L Au when made up to volume. The pH was then raised to 7 with NaOH solution, and the solution made up to 100 mL final volume, and stored in glass in the dark. The final solution was expected to contain 10 mM $I^-$ and 10 mg/L Au (less any metal precipitated). The actual measured concentration was 9.0 mg/L Au. NB. Ag was not added to this solution because of the very low solubility of AgI.

### 2.2.4. Chloride Complex.

14.61 g NaCl (58.44 g molecular weight) was mixed with approximately 100 mL deionized water, then Au and Ag standards were added so as to give final Au and Ag concentrations of 10 mg/L when made up to volume. The solution was made up to 250 mL final volume, and stored in glass. The final solution was expected to contain one mole/L (M) $Cl^-$ and 10 mg/L Au and Ag (less any metal precipitated), and have a pH below 3. Actual measured concentrations were 9.0 mg/L Au and 8.0 mg/L Ag.

## 2.3. Addition of Solutions to Soils.

Humate, Thiosulphate and Iodide.

Fifty grams of soil were weighed into a 350 mL glass bottle and 90 mL of deionized water added. Following this, 10 mL of the solution was added, the bottle sealed and placed on an automatic shaker in the dark. The initial concentration of the ligands, and the Au $\pm$ Ag in the mixtures, was 0.1 times that of the stock solution.

Chloride.

A series of soil/water mixtures were prepared to simulate the interaction of Au- and Ag-rich acid saline waters with soil. Fifty grams of soil were weighed into a 350 mL glass bottle and 50 mL of 1 $\underline{M}$ NaCl solution added. Sufficient HCl was added to ensure the mixture had a pH below 4 even after several days equilibration (this required considerable acid for samples 1468 and 1470), and then 10 mL of the Au/Ag chloride stock solution was added. The solution was made up to 100 mL with 1 $\underline{M}$ NaCl, the bottle was sealed and placed on an automatic shaker in the dark. The initial concentration of the Au and Ag was 0.1 times that of the stock solution, with Cl⁻ concentration of about 1 $\underline{M}$, and a pH < 4.

Adsorption.

A series of soil/water mixtures was prepared to observe the effect of adsorption of 'uncomplexed' Au and Ag onto the soils. Fifty grams of soil were weighed into a 350 mL glass bottle and 90 mL of deionized water was added. Gold and Ag were added as concentrated standards to yield a solution of 1 mg/L Au and Ag in a dilute Cl⁻ solution. The mixture was made up to 100 mL with deionized water, and the bottle then sealed and placed on an automatic shaker in the dark.

No attempt, other than normal clean laboratory practice, was made to exclude organisms during preparation and bottling of the mixtures. It is thus feasible that "exotic" bacteria could contaminate the mixtures. However, it is more likely that most organisms present in the mixtures would have been derived from the samples themselves, which would be expected to have significant *in situ* biota concentrations.

After two weeks, and after three months, the bottles were opened and 10 mL aliquots of the mixtures were taken. The aliquots were centrifuged, filtered through 0.45 μm millipore, and the filtrate digested with aqua-regia. The solution was then made up to 10 mL in 1 $\underline{M}$ HCl / 0.3 M HNO$_3$ for analysis for Au and Ag by ICP-MS. Subsamples of the various Au$\pm$Ag solutions (Section 2.2) were also analysed in the same manner, so as to provide a direct comparison for determination of the amount of Au and Ag removed from solution.

## 3. Results and Discussion

### 3.1. Tabulated Data

Data for the sorption experiments are given in Tables 3 and 4.

Table 3: Sorption Results for Au

| Complex | Initial Conc. (µg/L) | Time | Percentage Remaining in Solution | | | | | | |
|---------|------|------|------|------|------|------|------|------|------|
| | | | Moss | 1467 | 1468 | 1470 | Std. 7 | MKD | OB |
| Humic | 340 | 2 weeks | 40 | 1 | 1 | 1 | 3 | 1 | 3 |
| | | 3 months | 24 | 3 | 0.3 | 14 | 0.3 | 9 | 8 |
| Thiosulphate | 850 | 2 weeks | 17 | 6 | 10 | 63 | 25 | 1.0 | <0.5 |
| | | 3 months | 19 | <0.1 | 0.3 | 9 | <0.1 | <0.1 | <0.1 |
| Iodide | 900 | 2 weeks | 11 | 7 | 1 | 1 | 1 | 1 | 67 |
| | | 3 months | 24 | 31 | 51 | 24 | 3 | 0.7 | 55 |
| Chloride | 900 | 2 weeks | 2 | 3 | 2 | 1 | 4 | 1 | 36 |
| | | 3 months | <1 | <1 | nd | nd | <1 | <1 | <1 |
| Water | 1000 | 2 weeks | 1 | 2 | 0.5 | 2 | 1 | 5 | 0.5 |
| | | 3 months | 5 | 26 | 20 | 9 | <0.1 | 2 | <0.1 |

nd    not determined (due to breakages of the bottles).

Table 4: Sorption Results for Ag.

| Complex | Initial Conc. (µg/L) | Time | Percentage Remaining in Solution | | | | | | |
|---------|------|------|------|------|------|------|------|------|------|
| | | | Moss | 1467 | 1468 | 1470 | Std. 7 | MKD | OB |
| Humic | 255 | 2 weeks | 24 | 4 | 4 | 4 | 6 | <2 | 6 |
| | | 3 months | 16 | <0.4 | <0.4 | <0.4 | 0.8 | <0.4 | <0.4 |
| Thiosulphate | 880 | 2 weeks | 13 | 1 | <0.6 | 45 | 1 | 0.6 | <0.6 |
| | | 3 months | 16 | 0.2 | <0.1 | 1 | 0.1 | <0.1 | <0.1 |
| Chloride | 800 | 2 weeks | 4 | 93 | 100 | 98 | 100 | 96 | 100 |
| | | 3 months | <1 | 38 | nd | nd | 44 | 53 | 59 |
| Water | 1000 | 2 weeks | 2 | 2 | 1 | 1 | 2 | 1 | 2 |
| | | 3 months | 8 | 0.8 | 0.2 | <0.1 | <0.1 | <0.1 | <0.1 |

nd    not determined (due to breakages of the bottles).

Direct comparisons of the behaviour of Au and Ag are shown in Figs. 1 to 10, which best illustrate the experimental results. Data will be discussed for each separate complex (Sections 3.2.1 - 3.2.5) and then summarized in Section 3.3.

## 3.2. Discussion of Results for Each Complex

### 3.2.1. Humic Complex

After two weeks of shaking, more than 90% of the Au and Ag from the humate solution has been sorbed onto the soils in all of the mixtures, with the notable exception of the mixture with Peat Moss (Fig. 1). Silver is marginally more soluble than Au in these mixtures, again with the exception of the Peat Moss mixture. This would suggest that the humic complexes with Au and Ag are not strong and that Au and Ag humate is readily

immobilized. The lesser sorption of the Au and Ag by the Peat Moss is possibly because the competition for Au and Ag is only between soluble humic matter and solid organic matter, in the absence of other soil minerals (*e.g.* Fe oxides, carbonates, Mn oxides) that are present in the other soils.
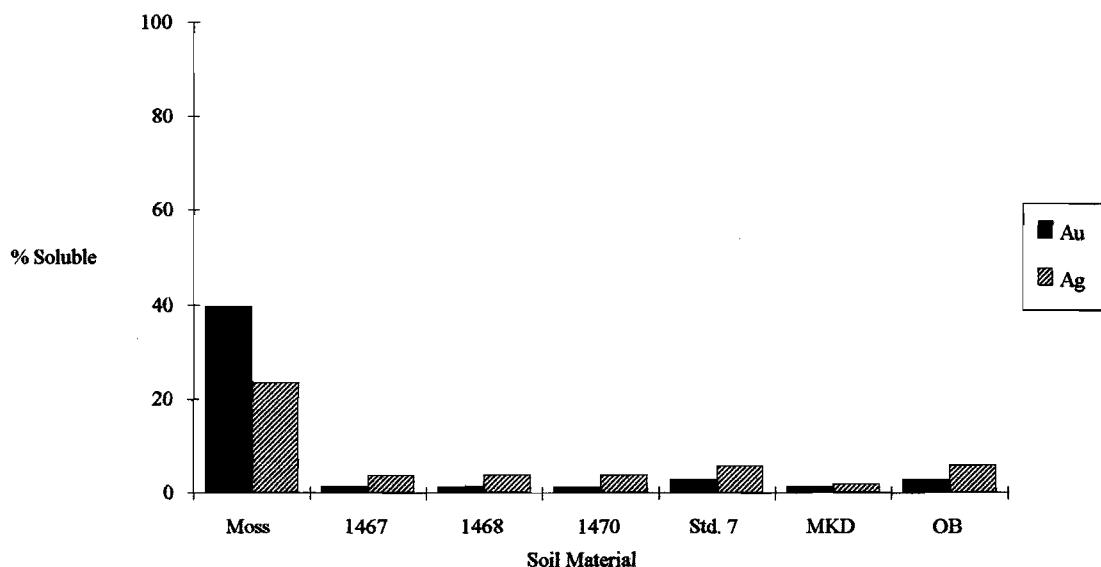


Figure 1: Concentration of Au/Ag Humate Complexes in Contact with Various Soils after Two Weeks.

After three months, at the conclusion of the experiment, some significant variations are observed (Fig. 2). Although Au and Ag still have a significant solubility in the Peat Moss mixture, their concentrations in solution have decreased to about 70% of those observed at 2 weeks. For the other soils, Ag has been virtually totally sorbed. The concentration of soluble Au is very low in the mixtures with 1468 and Std. 7, both of which are Fe-rich (Table 1). However, in the other mixtures, the concentration of soluble Au has increased significantly implying that Au had first been sorbed and later redissolved. Mechanisms causing this could include alteration of the soluble humate into a form which dissolves Au more strongly, or release of chemicals from the soil itself that are able to dissolve Au. The soils that show redissolution of Au are 1470, MKD and OB, which contain little organic matter (Table 1), and would not be expected to be biologically active. Materials which have greater organic contents, such as 1467 and 1468, show significant redissolution of Au in iodide solution (Section 3.2.3) and in water (Section 3.2.5), but very little in the humic mixtures. Therefore, it appears that redissolution of Au occurs as a result of biological reactions with the soluble humic matter that is being added. However, further work would be required to verify this mechanism adequately.

The important observations for the Au/Ag humate tests are:

(i)  the low concentrations of Au and Ag humate complexes in solution, with the exception of Peat Moss;

(ii)  the redissolution of sorbed Au (with Ag maintained in the solid) over time, in a manner significantly different from that for Au added either as the iodide complex or in water.
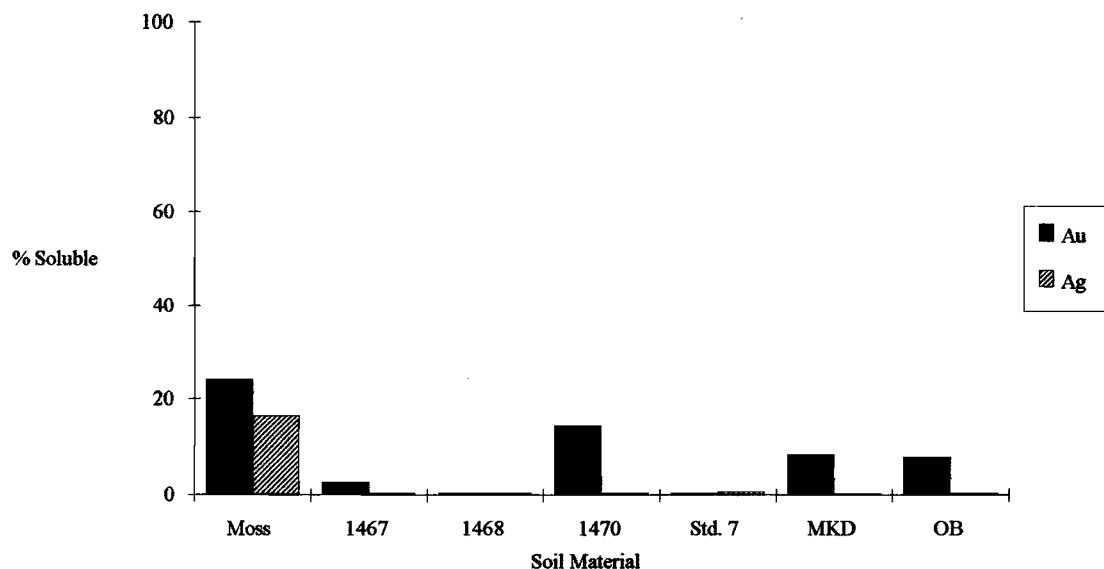
Figure 2: Concentration of Au/Ag Humate Complex in Contact with various Soils after Three Months.

Note, however, that there are other biologically derived species, such as cyanide or amino acids, that may mobilize Au more strongly than humate, and that Au and Ag could still have high mobilities in organic-rich soils, due to the influence of these species.

### 3.2.2. Thiosulphate Complex

After two weeks of shaking, the Au/Ag thiosulphate solutions with the various solids (Fig. 3) show a greater mobility than Au/Ag humate complex (Fig. 1). Gold and Ag are most soluble when the thiosulphate solutions are in contact with carbonate-rich soil 1470, and also have significant dissolved concentrations when in contact with Peat Moss. In both cases, Au is more soluble than Ag. This is even more marked for the mixtures containing soils 1467, 1468 and Std. 7, for which Au still has a moderate solubility after 2 weeks (dissolved Au = 6 - 25%), whereas Ag is very strongly sorbed (dissolved Ag $\leq$ 1%). However, there is still a general similarity in the solubility of Au and Ag thiosulphate complexes, which is consistent with the formation of Ag-rich secondary gold, where the major transport mechanism is postulated as being the thiosulphate complex (Webster, 1984; 1986).

The two samples with the lowest thiosulphate Au solubility are MKD and OB, which both contain significant levels of Mn oxides (Tables 1 and 2). This is consistent with results obtained by Webster and Mann (1984) on the Upper Ridges mine near Wau, in Papua New Guinea, backed by laboratory studies Webster, 1986), which indicated that Au and Ag thiosulphate are immobilized by adsorption on Mn oxides. This marked low mobility of both Au and Ag thiosulphate in contact with Mn oxides may explain the formation of Ag-rich secondary gold, without needing to postulate mixed Au/Ag thiosulphate complexes (Webster, 1986).

After three months there are marked changes observed in the concentrations of dissolved Au and Ag (Fig. 4). Concentrations are marginally increased in the solution shaken with the Peat Moss, again indicating the low affinity of Au for solid organic matter. The concentration with the carbonate-rich sample 1470, although still moderately high, is strongly reduced from the levels observed at 2 weeks (Fig. 3), suggesting
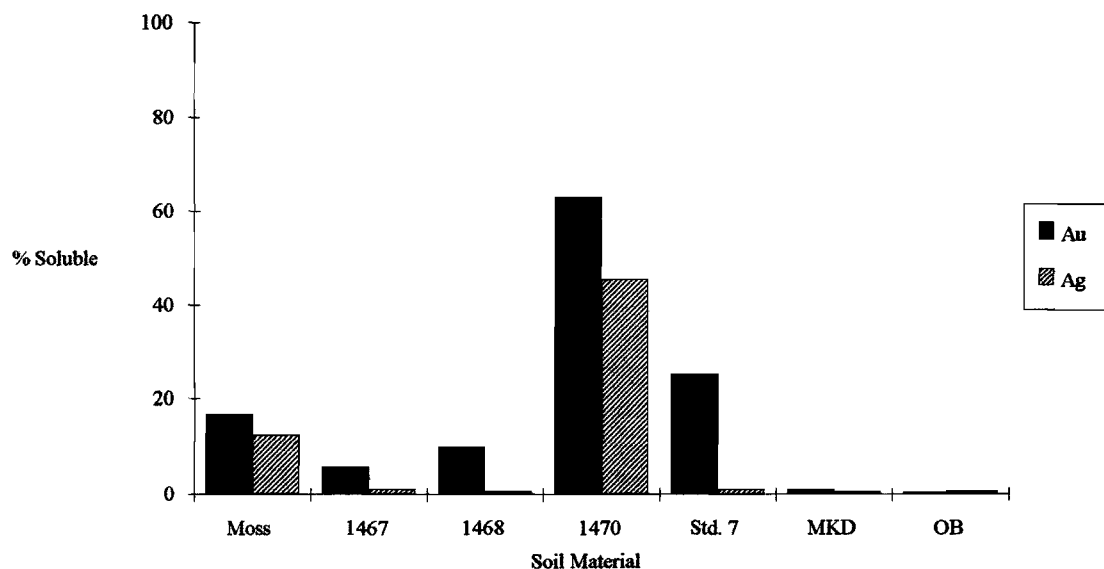
Figure 3: Concentration of Au/Ag Thiosulphate Complex in Contact with various Soils after Two Weeks.

sorption reactions are slow. Concentrations of dissolved Au and Ag are all 0.3% or lower for the solutions shaken with 1467, 1468, Std. 7, MKD and OB for 3 months, compared to the moderate concentrations present after 2 weeks. The results imply that the sorption reaction is kinetically slow, rather than that the Au thiosulphate has a high equilibrium concentration when in contact with these soils.
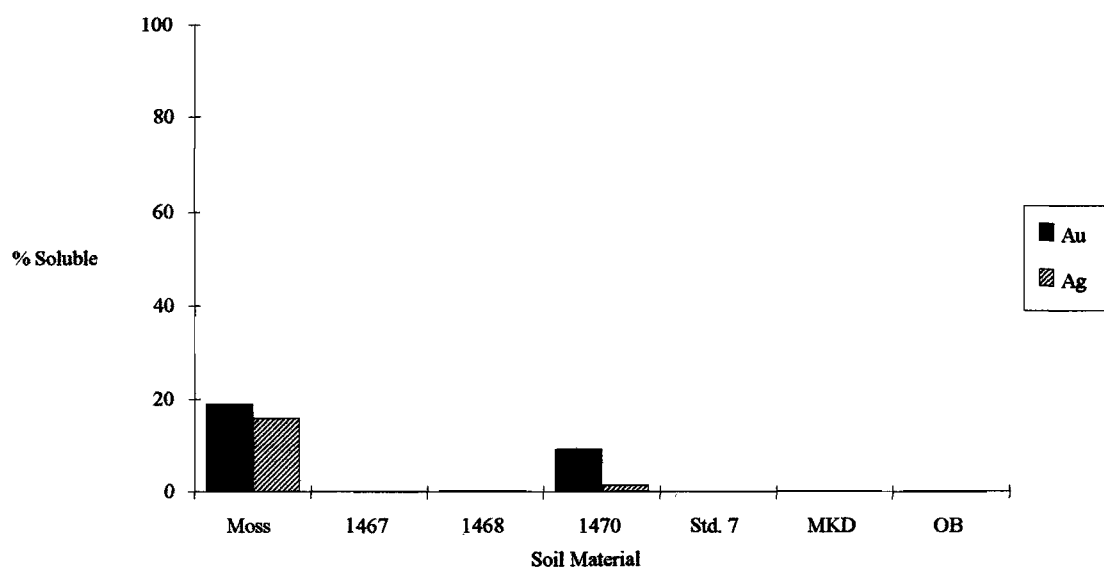


Figure 4: Solubility of Au/Ag Thiosulphate Complex in Contact with various Soils after Three Months.

The concentrations of dissolved Au and Ag for the thiosulphate solutions shaken with soils for 3 months are significantly lower than those observed for solutions of Au and Ag in an uncomplexed form shaken with soils

(Section 3.2.5; Fig. 10). This implies that the thiosulphate complexes are sorbing in a form that is not readily redissolved. It is not yet clear how this occurs. Possibilities are that the Au thiosulphate complex is being decomposed to a Au-S compound of low solubility, or that the decomposition of the Au-thiosulphate complex results in the chemical reduction of the Au.

In summary, the general characteristics of the Au and Ag thiosulphate complexes are:

(i)   Au and Ag behave similarly but Au has a greater solubility under the experimental conditions;
(ii)  Au is initially highly soluble, which appears to be due to slow sorption;
(iii) Au and Ag thiosulphate are least mobile when in contact with Mn minerals;
(iv)  Solid organic matter, on its own, only partially immobilizes Au and Ag;
(iv)  the Au thiosulphate complex is sorbed in a form that is not readily redissolved.

### 3.2.3. Iodide Complex

Only the Au iodide complex has been tested, due to the low solubility of Ag iodide. After 2 weeks of shaking (Fig. 5), Au iodide remains most soluble when in contact with the Mn-rich OB sample. This trend is also observed for Au chloride (Section 3.2.4), implying this to be a general phenomenon for Au halides. The OB solid contains the most Mn (calculated $MnO_2$ = 12.7%; Table 1). Laboratory studies on the dissolution of Au chloride (Cloke and Kelly, 1964; Miller and Fisher, 1973) have indicated the importance of $MnO_2$ in the dissolution of Au, due to the high oxidation potential of the $Mn^{2+}/MnO_2$ couple. This has been inferred in field studies on the oxidative control of Au chloride and Au iodide dissolution in groundwater (Gray, 1990b). The sample containing the greatest Mn will be most able to maintain sufficiently oxidizing conditions for Au iodide or chloride to be soluble. At present it is not clear why the second highest Mn sample, MKD, does not show this effect. Some possible reasons are that MKD is substantially lower in Mn than OB and that the Mn is occluded or in some manner 'deactivated' from raising the Eh of the solution, or that cryptomelane (present in OB, but not MKD) may be more effective than lithiophorite (present in both of the samples) in maintaining oxidizing conditions.
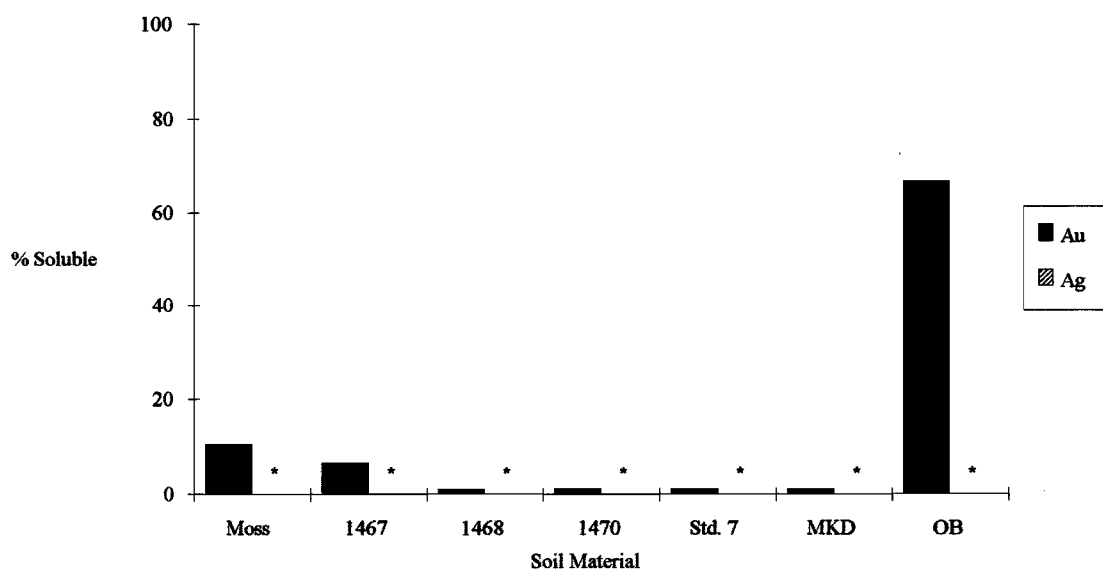


Figure 5: Concentration of Au Iodide Complex in Contact with various Soils after Two Weeks.

After 3 months of shaking (Fig. 6), the OB mixture still contains high amounts of soluble Au. In contrast, significant amounts (24 - 51%) of the Au that was sorbed at 2 weeks in the Peat Moss, 1467, 1468 and 1470 mixtures have been redissolved, with even a small amount (3%) redissolved for the Std. 7 mixture. These observations of Au redissolution can be directly compared with previous work on the shaking of Au with soils 1467, 1468 and 1470, as discussed in Gray *et al.* (1990a). This redissolution is thought to be due to biological activity because it was reduced when the soil mixtures were sterilized by irradiation. This is also consistent with sample MKD not showing any redissolution of Au. Unlike samples 1467, 1468, 1470 and Std. 7, sample MKD is not derived from a surface soil horizon and contains very little organic matter (< 0.05, Table 1), and would therefore be expected to have a low biological activity due to a shortage of nutrients.
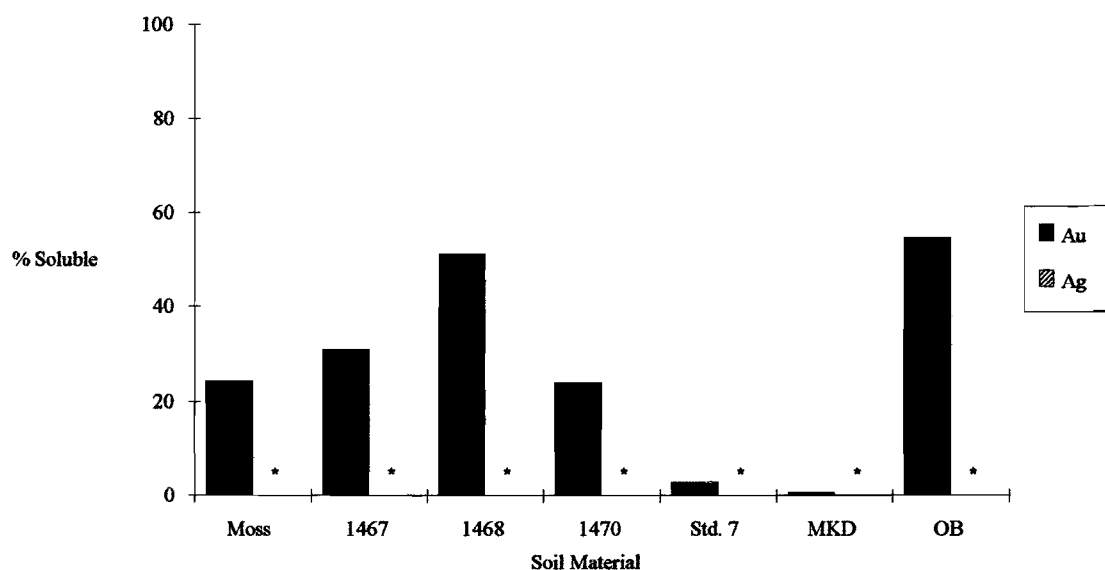


Figure 6: Concentration of Au Iodide Complex in Contact with various Soils after Three Months.

The major observations for the iodide solutions are:

(i)  Au in the iodide solution is highly mobile when contacting the Mn rich OB material, and is strongly sorbed by the other soils;

(ii)  The Peat Moss, 1467, 1468 and 1470 mixtures show major redissolution of the sorbed Au after 3 months, possibly because of biological production of ligands.

### 3.2.4. Chloride Complex

The chloride solution/soil mixtures were prepared using acid (pH < 4), saline (Cl⁻ concentration approximately 1 M) solutions to simulate interaction of soil or weathered material with acid/saline waters. After 2 weeks (Fig. 7), Au and Ag have very different solubilities under these experimental conditions. With the exception of the Peat Moss mixture, sorption of Ag is very minor, whereas Au is strongly sorbed by all of the soil mixtures, with the exception of the OB sample (as discussed in Section 3.2.3). After 3 months shaking (Fig. 8), Au is virtually totally sorbed in all of the mixtures analysed, whereas Ag still has a high solubility. This greater solubility

of Ag and high sorption of Au is entirely consistent with the previous discussion on the geochemical separation of these two elements during weathering (Mann, 1984).
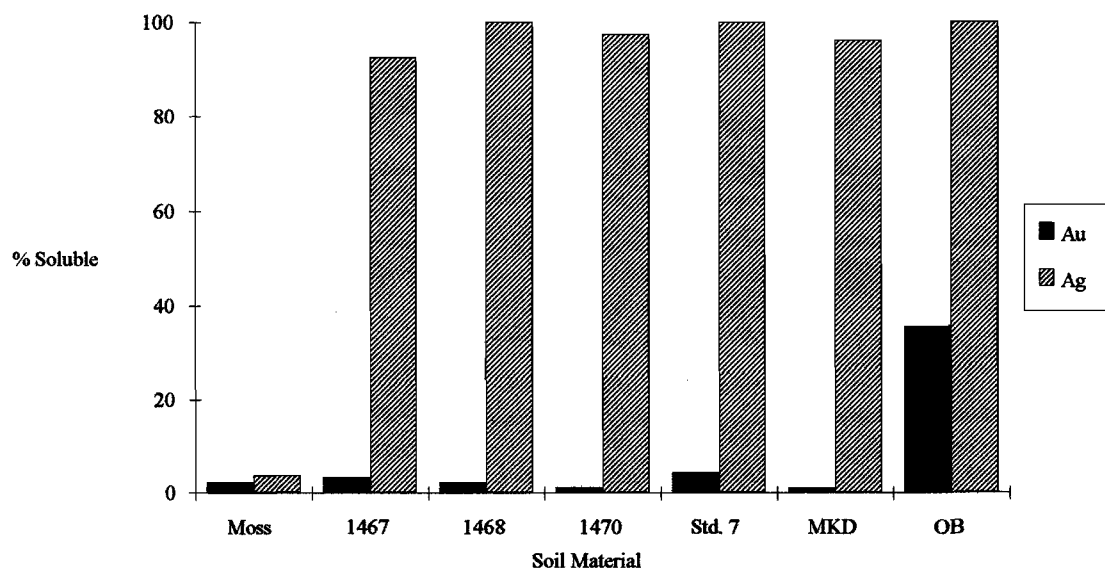


Figure 7: Solubility of Au/Ag Chloride Complex in Contact with various Soils after Two Weeks.

No redissolution of Au was observed after 3 months (Fig. 8), unlike the humate (Fig. 2), iodide (Fig. 6) or uncomplexed mixtures (Fig. 10). This could be due to acidification suppressing biological activity or because other potentially important Au ligands, such as thiosulphate or the S-containing amino acid cysteine (Korobushkina et al., 1983), are unstable in acid conditions.
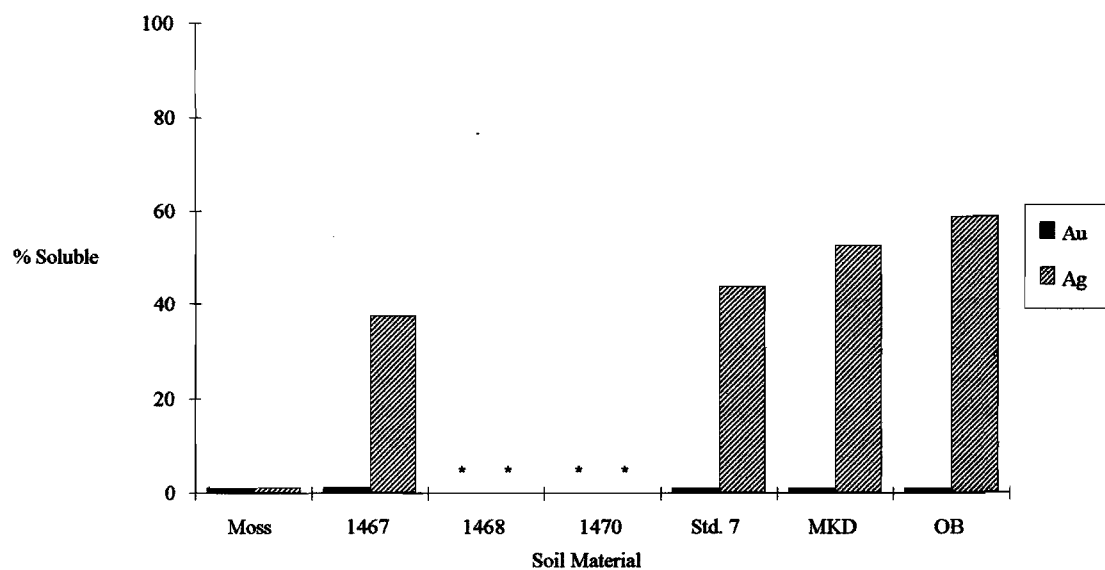


Figure 8: Solubility of Au/Ag Chloride Complex in Contact with various Soils after Three Months. Asterisks indicate that solubility has not been determined.

Thus, the behaviour of Au and Ag in the chloride solution is markedly different from that for the other ligands tested, in that:

(i)   Ag is much more soluble than Au, being sorbed only when in contact with the Peat Moss;

(ii)  Au is soluble only when in contact with the Mn-rich sample OB, as with the iodide complex;

(iii) there is no redissolution of sorbed Au during the experiment, possibly due to suppression of biological activity by saline and/or acid conditions.

### 3.2.5. Uncomplexed System

Shaking diluted Au and Ag standards with the soils (Section 2.3) will presumably result initially in a solution in which the Au and Ag will be very weakly complexed by the small amounts of chloride present (calculated to be approximately 2.5 m$\underline{M}$, or 100 mg/L). After 2 weeks shaking of the mixtures (Fig. 9) the Au and Ag are, as expected, virtually totally sorbed. After 3 months (Fig. 10) significant redissolution of the Au is observed for the Peat Moss, 1467, 1468 and 1470 mixtures. Silver was only redissolved in the Peat Moss mixture. Thus, the redissolution mechanism appears to be strongly specific to Au. The observed redissolution pattern was very similar to that for the iodide mixtures (Fig. 6), suggesting similar mechanisms in both cases, as discussed in Section 3.2.3.
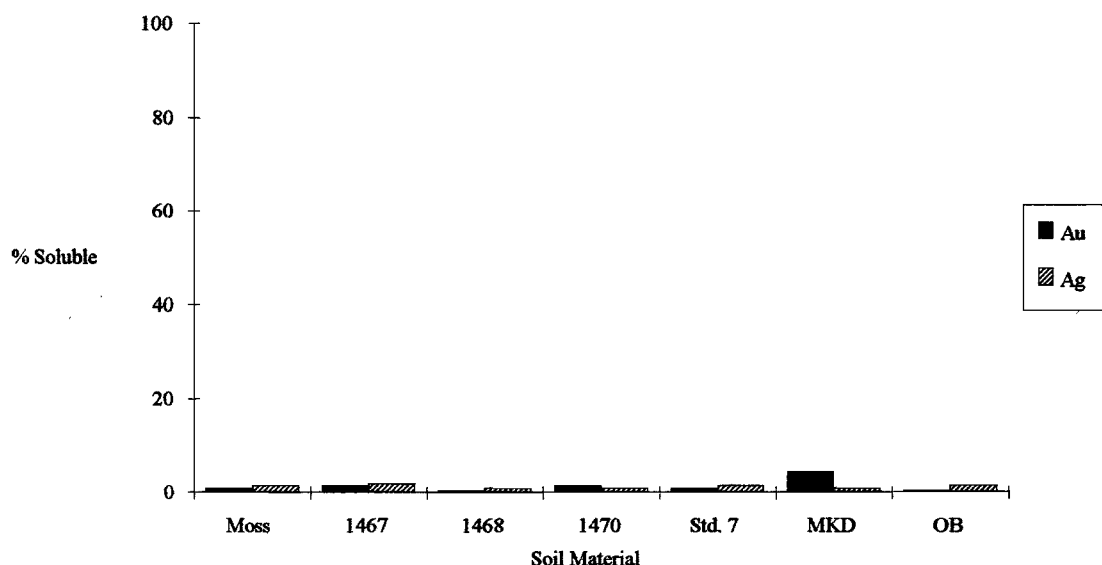


Figure 9:  Concentration of Au/Ag in Water in Contact with various Soils after Two Weeks.

The critical observations for the uncomplexed system were:

(i)   the high sorption of Au and Ag;

(ii)  the significant redissolution of Au, but (with the exception of the Peat Moss mixture) not Ag, after 3 month shaking, presumably due to release of ligands by the soil itself;

(iii) the similarity in the redissolution of the Au when added in the uncomplexed form, and when added as the iodide complex.
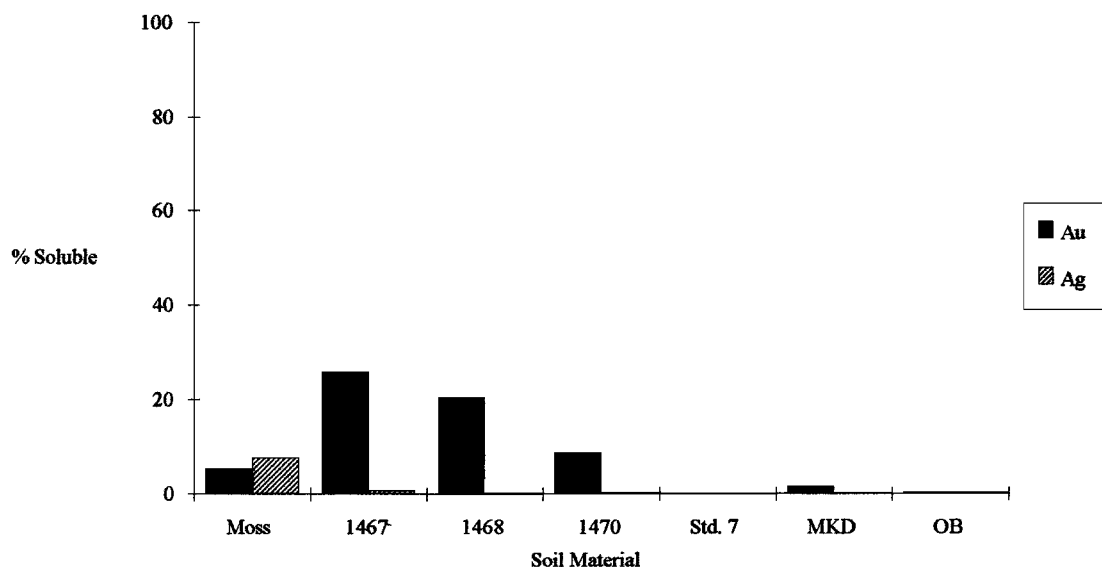
Figure 10: Concentration of Au/Ag in Water in Contact with various Soils after Three Months.

## 3.3. Discussion

### 3.3.1. Thiosulphate

Thiosulphate is generated during neutral to alkaline weathering of sulphides (Listova *et al.*, 1966; Granger and Warren, 1969; Goldhaber, 1983; Mann, 1984; Webster, 1984). Thus, thiosulphate complexation of Au and Ag represents a remobilization mechanism that would occur at depth in deeply weathered environments. Results from this experiment (Section 3.2.2) indicate that the Au and Ag thiosulphate complexes are only slowly sorbed by organic, Fe oxide or carbonate rich materials, but are strongly sorbed by Mn oxides. Gold and Ag have similar mobilities, with Ag being the less soluble under the various conditions tested. These results strongly support the hypothesis that Au mobilized as the thiosulphate complex tends to be immobilized by Mn oxides and to have secondary forms rich in Ag (Webster, 1984, 1986; Webster and Mann, 1984). Although Au and Ag are ultimately immobilized after three months in most of the mixtures, the slow kinetics of the sorption reaction could still allow for significant mobilization of Au as the thiosulphate complex in soils.

### 3.3.2. Chloride

A number of texts have indicated the importance of the Au chloride complex in the mobilization of Au in acid/saline environments. Results discussed in this report (Section 3.2.4) suggest that Au chloride tends to have a low solubility, except in a Mn-rich regime. This is consistent with laboratory experiments (Cloke and Kelly, 1964; Miller and Fisher, 1973) and field observations (Gray, 1990b), indicating an important role for Mn in the solubilization of Au. The results also indicate that Ag is more soluble than Au in saline conditions, except in very organic-rich environments. This finding is consistent with the observation that weathering commonly causes loss of Ag (Mann, 1984).

It is significant that the thiosulphate and chloride complexes have (as expected) virtually opposite behaviours. Thus, the redistribution of Au will be critically dependent on the nature of the Au complex.

### 3.3.3. Iodide

The Au iodide complex was included as part of this experiment because field studies at the Panglo deposit, near Kalgoorlie, have indicated that iodide complexation of Au may dominate chloride in some saline groundwaters (Gray, 1990b). The Au iodide complex has a broadly similar sorption behaviour to Au chloride, except that it generally appears to be less sorbed. Therefore, if Au is present as the iodide, rather than the chloride, complex, it may have a greater mobility in many natural groundwaters than previously suspected.

### 3.3.4. Humate

Gold is presumably complexed by a number of biologically generated ligands in the soil environment. Only the humate ligand was explicitly tested in these experiments and results indicate that it solubilizes Au very poorly. These findings are in contrast with those of some other workers (Friese, 1931; Baker, 1973, 1978; Boyle et al., 1975) and is typical of the wide disparity in results noted for studies of the interaction between Au and organic matter Gray (1988). The observation that after three months the humic material appears to be producing chemical species capable of dissolving Au (Fig. 1; Section 3.2.1) suggests that some of these workers mentioned above (who generally conducted their dissolution experiments over a period of weeks or months) may have observed dissolution of Au by decomposed, rather than by fresh humic acid. It is also of interest that the mixtures showing appreciable redissolution of the Au included the two Mn rich samples MKD and OB, as this may indicate that Mn may play an important role in alteration of organic matter into forms capable of dissolving, possibly due to its high oxidative potential when present as the $Mn^{IV}$ ion. Investigations of the Au-humate interaction are continuing within the Weathering Processes Research Group, and further results are discussed in Gray et al. (1990b).

### 3.3.5. Gold Redissolution

The importance of biologically generated ligands is suggested by observations of the redissolution of precipitated Au. This is most clearly observed for the 'uncomplexed' Au and Ag (Section 3.2.5), which were added as dilute $Cl^-/NO_3^-$ solutions. The dissolved Au and Ag concentrations were very low after 2 weeks. However, after three months, significant proportions of the Au were redissolved. Presumably one or more chemical species had been formed by biological processes, and these species were able to dissolve Au. This phenomenon has been investigated in detail for samples 1467, 1468 and 1470 in Gray et al. (1990a). A very similar redissolution of Au was observed for the iodide mixtures (Section 3.2.3), possibly because the Au iodide is, like the 'uncomplexed' Au, precipitated in a form that is easily redissolved. The Au humate mixtures also show a redissolution of the Au, though with a very different pattern (Section 3.2.1). Possibly this is because the addition of soluble organic matter changes the concentration and types of organic matter in the soil/water mixtures. The Au thiosulphate complex, on the other hand, is sorbed by the soils in a manner that appears to preclude redissolution, whereas the lack of redissolution of the Au chloride is possibly due to the acid/saline conditions in the mixtures suppressing biological activity.

These results indicate a major capacity for soils to mobilize Au and maintain it in solution, presumably as a result of biological activity, when the soil is saturated with water over extended periods. The other critical observation for the redissolution phenomenon is that it generally occurred for Au alone, with Ag remaining immobilized. This implies either that Ag is being precipitated in a highly insoluble form, or that the ligands are highly selective for Au. The latter hypothesis seems more likely, and is possibly a function of the high affinity of

Au for chemically 'soft' ligands such as the those containing the sulphide (R-S⁻) group, which may be released as part of a number of soluble molecules during biological activity. Further work on soils, for both added and *in situ*. Au, that supports this hypothesis, is described in Gray *et al.* (1990a). In general, the work for these two reports implies that in biologically active soils, Au should be considered a mobile element, rather than as a noble metal.

# 4. Conclusions

The differing behaviours of the various Au and Ag complexes demonstrate the critical influence of the chemical complexation of Au on its mobility within the soil profile.

Humate complexes were found to maintain only small concentrations of Au in solution, suggesting a weak interaction between Au and humate.

Gold and Ag thiosulphates had a high initial mobility when contacting most of the soils, with the exception of the Mn rich materials which quickly sorbed both the Au and Ag. In general, both Au and Ag had similar mobilities. When finally immobilized, Au did not redissolve.

In a chloride-rich solution, Au was more highly sorbed on soils than Ag, only having an appreciable solubility when in contact with Mn-rich material. Gold iodide had a similar sorption pattern.

'Uncomplexed' Au and Ag were readily sorbed by the soils but after three months, a number of the 'uncomplexed' mixtures contained significant quantities of dissolved Au (but not Ag). This is possibly due to soluble species with a high affinity for Au produced by biological activity. Very similar effects were also observed for Au iodide. The humate mixtures also showed appreciable redissolution of Au, though in a different manner to the uncomplexed and the iodide mixtures, possibly due to the different organic composition of the solutions.

The redissolution of Au via species released from the soil suggest that similar mechanisms may be conducive to Au mobility in natural soils, and this may be an important mechanism for soil Au redistribution.

# Acknowledgements

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