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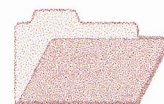
Cooperative Research Centre for
Landscape Evolution & Mineral Exploration



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THE AQUEOUS CHEMISTRY OF GOLD IN THE WEATHERING ENVIRONMENT

D.J. Gray

CRC LEME OPEN FILE REPORT 38

September 1998

(CSIRO Division of Exploration Geoscience Report 4R, 1988.
Second impression 1998)

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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.

This report (CRC LEME Open File Report 38) is a first revision of CSIRO, Division of Exploration Geoscience Restricted Report 004R, first issued in 1988, which formed part of the CSIRO/AMIRA Projects P240 and P241.

Copies of this publication can be obtained from:

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PREFACE

The CSIRO - AMIRA project "Exploration for Concealed Gold Deposits, Yilgarn Block, Western Australia" has as its overall aim the development of improved geological, geochemical and geophysical methods for mineral exploration that will facilitate the location of blind, concealed or deeply weathered gold deposits. This Report presents results of research conducted as part of Module 2 of this project (AMIRA Project 241): "Gold and Associated Elements in the Regolith - Dispersion Processes and Implications for Exploration".

The objectives of this Module are:

- I. To obtain a better understanding of the nature and genesis of lateritic and supergene gold deposits.
- II. To determine characteristics useful for exploration, especially in areas of transported overburden, for:
 - a. further lateritic and supergene deposits, and
 - b. primary mineralization - including that with no expression as appreciable secondary mineralization.
- III. To increase knowledge of the properties and genesis of the regolith.
- IV. To provide data applicable for exploration for other commodities in and beneath the regolith.

In particular, this work covers an investigation and critique of literature of the chemistry and geochemistry of gold during weathering, with additional calculations of potentially important geochemical regimes for the mobilization of gold, and has been of importance in:

- i. Suggesting the important geochemical and mineralogical associations of gold in and close to lateritic and supergene gold mineralization, in a variety of geological, geomorphological and regional environments.
- ii. Suggesting other elements that may be associated with gold in the weathering profile.

In general, conclusions from thermodynamic data are given in the main text while the thermodynamic database and calculations are presented in the appendices. It should be noted that some of the thermodynamic data used in this report arise from single and/or unverified sources. Where conclusions have been drawn using such data it is noted in the relevant section of the text.

This report is designed to provide background information for understanding the processes involved in the mobility of gold during weathering and as a guide for further work on the chemistry of gold. An understanding of the thermodynamics of gold associated with ligands such as chloride, thiosulfate and cyanide is an essential precursor for such work.

ABSTRACT

Literature on the chemistry of gold in the weathering environment was critically examined. Additional thermodynamic data were calculated by the author to test and clarify conclusions drawn by other workers. New hypotheses on some of the mechanisms of gold mobility and alteration were also advanced.

Section 2 gives a brief summary of gold primary mineralization and associated minerals. Section 3 gives relevant information on weathering processes and methods of analysis of thermodynamic data. The weathering environments under which the thermodynamically unstable thiosulfate and sulfite anions (which are effective ligands for gold) can be generated are discussed. An explanation of the importance of solution characteristics such as Eh, pH, and the presence of ligands such as thiosulfate or chloride for the mobilization of gold is also given. It is demonstrated in section 4 that gold can be mobile in particular environments: either ligated by inorganic anions such as chloride, thiosulfate or cyanide; as a colloid; or under biological influence. These mobilized forms of gold may be precipitated from solution by a number of mechanisms: changes in solution chemistry; reactions with metal ions in solution; adsorption onto the solid phase; or decomposition of ligand molecules. This is dealt with in section 5.

The later sections of this report present a more general overview of gold chemistry in the weathering environment. Section 6 discusses the observed increases in gold fineness in the weathering zone and how this will be influenced by the form of the aqueous gold species: thus, for example, equilibration of gold and silver with a chloride rich solution will precipitate very high fineness gold; while the presence of thiosulfate in solution will result in electrum of lower fineness. Section 7 discusses alteration of primary gold grains: in particular a theory of galvanic silver loss, whereby gold and silver are leached from electrum grains and gold is redeposited on the same grain, is suggested for the widespread occurrence of low silver rims in the weathering zone. Section 8 discusses the hypothesized environments of gold redistribution and the gold species that are considered to be important in each environment, as below:

<u>Environment</u>	<u>Gold Species</u>
Sulfide Weathering	$\text{Au}(\text{HS})_2^-$ $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$
Laterite and Soil	$\text{Au}(\text{CN})_2^-$ gold-organic matter gold colloids
Capillary Zone Arid/Acid Conditions Arid/Alkaline Conditions	AuCl_4^- and AuCl_2^- $\text{Au}(\text{OH})_2^-$

Further work on gold dissolution and re-precipitation, that may lead to a better understanding of the geochemistry of gold during weathering and in developing exploration strategies, is suggested in section 9. Much of this work will be initiated by the author shortly.

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1. INTRODUCTION

The investigation of the geochemistry of gold during weathering is of fundamental importance in:

- a) understanding and developing exploration strategies for
 - (i) alluvial and placer deposits,
 - (ii) lateritic and supergene deposits,
 - (iii) concealed primary deposits;
- b) obtaining a theoretical understanding of the processes of gold alteration, mobility and association.

Gold is a noble metal and generally is insoluble in aqueous solution, in the absence of complexing molecules. Gold concentrations in natural waters have been determined to be in the range of 0.1 to 500 ng/L (parts per trillion) in natural waters and 100 ng/L and greater in gold enriched waters (Chernyayev *et al.*, 1969; Baranova *et al.*, 1977; Hamilton *et al.*, 1983; McHugh, 1984). Various authors have described redistribution of gold in weathering profiles (Yassoglou and Nobeli, 1968; Boyle, 1979; Evans, 1981; Mann, 1984a,b; Smith and Keele, 1984; Wilson, 1984; Davy and El-Ansary, 1986; Freyssinet *et al.*, 1987; Michel, 1987), and in the zone of supergene alteration (Webster and Mann, 1984; Martini, 1986; Stoffregen, 1986). Gold is also taken up by a number of plants and other organisms (Razin and Rozhkov, 1966; Shacklette *et al.*, 1970; Kaspar *et al.*, 1972; Girling *et al.*, 1979; Warren, 1982; Smith and Keele, 1984; Smith and Hunt, 1985; Erdman and Olson, 1985; Dunn, 1986; Huang, 1986) and it has been suggested that use of plants in gold prospecting can complement or replace other geochemical methods.

Such data shows that gold should not only be considered a resistate element, as redistribution reactions can either concentrate or disperse gold in the weathered zone. An understanding of gold mobility in various environments would be useful in following the sequence of gold dissolution, precipitation and alteration that occur during particular weathering and landscape development processes. An understanding of these mechanisms and the role played by the parent material, pedological reactions and climate is critical in expanding the potential for geochemical prospecting for gold in areas covered by laterite, soil or other overburden.

2. GOLD IN THE UNWEATHERED ZONE

2.1 Gold Mineralization

The initial state of the gold and associated minerals effects the reactivity of the gold and the geochemical and hydrochemical conditions expected during supergene alteration. The minerals of gold are given in Table 1.

The most common gold minerals are native gold (Au) and gold telluride (AuTe₂), and these two groups will be discussed below (sections 2.2 and 2.3). Additionally, certain minerals (e.g. pyrite, quartz) are almost always found associated with gold mineralization. As described below, the presence of pyrite in particular may affect the geochemistry of gold during weathering and supergene alteration.

Table 1: Gold Minerals (from Boyle, 1979).

Native elements, alloys and metallic compounds

Gold	Au
Argentian gold (electrum)	(Au,Ag)
Cuprian gold (cuproauride)	(Au,Cu)
Palladian gold (porpezite)	(Au,Pd)
Rhodian gold (rhodite)	(Au,Rh)
Iridic gold	(Au,Ir)
Platinum gold	(Au,Pt)
Bismuthian gold	(Au,Bi)
Gold amalgam	Au ₂ Hg ₃ (?)
Maldonite	Au ₂ Bi
Auricupride	AuCu ₃
Palladium cuproauride	(Cu,Pd) ₃ Au ₂

Sulfide

Uytenbogaardite	Ag ₃ AuS ₂
-----------------	----------------------------------

Tellurides

Calaverite	AuTe ₂
Krennerite	(Au,Ag)Te ₂
Montbrayite	(Au,Sb) ₂ Te ₃
Petzite (antamokite)	Ag ₃ AuTe ₂
Muthmannite	(Ag,Au)Te
Sylvanite	(Au,Ag)Te ₄
Kostovite	AuCuTe ₄
Nagyagite	Pb ₅ Au(Te,Sb) ₄ S ₅₋₈

Antimonide

Aurostibite	AuSb ₂
-------------	-------------------

Selenide

Fischesserite	Ag ₃ AuSe ₂
---------------	-----------------------------------

Tellurate

Gold tellurate (?)	
--------------------	--

2.2 Native Gold

Native gold crystallizes in a great variety of forms (Boyle, 1979), the most common being parallel groups and twinned aggregates branching at 60 degrees parallel to the edges or the diagonals of the faces of (111); also commonly reticulated, dendritic, arborescent, filiform, wiry, mossy and spongy. Massive forms include rounded fragments (nuggets), flattened grains, scales, spangles, sprigs and finely divided particles (flour gold, mustard gold and paint gold). The size of gold particles in epigenetic gold-bearing deposits varies widely, the usual range being from less than 30 mg up to masses of 30 kg or more. In many deposits gold is present in an finely divided form in sulfides, sulfosalts or gangue minerals such as quartz.

In some deposits native gold is relatively pure, but in general it contains alloyed silver, and sometimes copper. In addition, one or more of the following elements may be present: Li, Na, K, Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Sc, Si, Ge, Sn, Pb, Ti, Zr, As, Sb, Bi, V, Se, Te, Cr, Mo, W, Mn, Co, Ni, Rh, Pd, Ir, Pt, U, Th and rare earths (Boyle, 1979). Most of these elements are present as mineral

inclusions (*ibid.*; Desborough *et al.*, 1971), and because they are generally present only as trace constituents (Antweiler and Campbell, 1977) then, to a close approximation

$$\text{Au} + \text{Ag} + \text{Cu} = 100 \%$$

in a gold nugget. The purity of native gold is generally defined in terms of fineness, determined by the weight of the metals present, *i.e.*

$$\text{fineness} = 1000 \times \frac{\text{Au}}{\text{Au} + \text{Ag} (+ \text{Cu})}.$$

Thus, pure gold will be 1000 fine whereas gold with 50% (by weight) silver will be 500 fine. Where fineness is less than 800 the metal is generally called electrum (Palache *et al.*, 1944), though there is no strict definition, as gold and silver form a continuous solid solution. Note that as silver has a mass of 107.9 and gold has a mass of 197.0, then 50% silver by weight (for example) represents 65% silver in terms of atomic proportions.

The Au/Ag/Cu proportions are described as the gold 'signature' (Antweiler and Campbell, 1977). If native gold were unaffected by weathering processes then concentrations of Ag, Cu and trace elements would be a useful tool in geochemical exploration for gold. However, as indicated below (section 6), native gold is commonly modified during weathering, usually with an increase in fineness, and the gold signature in nuggets from weathered material should be interpreted carefully.

2.3 Gold Tellurides

Tellurium is very commonly associated with gold deposits. Gold tellurides probably occur in trace amounts in most primary deposits and in some deposits tellurides are important ore minerals of both gold and silver. The tellurides generally occur in quartz and quartz-carbonate veins and in pyritized, silicified and carbonated zones in volcanic hosted deposits.

Gold telluride (calaverite) is less stable (more soluble) than pure Au under oxidizing conditions (Mann, 1984b). On weathering gold precipitates as the metal and tellurium is adsorbed by iron oxides, possibly as the Te^{4+} or Te^{6+} cation. Thus, partly-weathered calaverite is commonly observed to be surrounded by secondary gold, and with some tellurium in nearby iron oxides (*ibid.*).

2.4 Associated Minerals

The two phases generally found intimately associated with gold are quartz and pyritic minerals.

Quartz is almost invariably associated with gold, as described in the old adage 'quartz is the mother of gold'. Boyle (1979) suggests "a marked relationship between gold and silicon" which "must reflect some fundamental parallel in the chemistries of the two elements, either in their solution or colloidal characteristics."

Sulfur is a constant associate of gold in all types of deposits, usually pyrite and arsenopyrite; chalcopyrite, galena, sphalerite, tetrahedrite-tennantite and stibnite are also commonly observed intimately associated with gold. Thus, other elements commonly associated with gold will be arsenic, copper, lead, zinc and antimony. The gold - sulfide association has particular importance for gold geochemistry during supergene alteration. Sulfide weathering causes high acidity of the groundwater, which can result in gold mobility. Alternatively, weathering of sulfide minerals may release thiosulfate or sulfite ions, which can complex gold, into solution. These factors are discussed in sections 3.3, 3.4, 4.4 and 4.5.

3. WEATHERING PROCESSES AND GOLD MOBILIZATION

3.1 Introduction

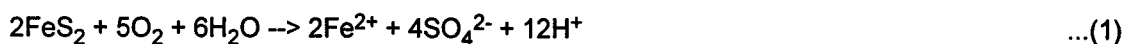
Weathering (Supergene Alteration) occurs as a mineral assemblage equilibrates with the terrestrial environment under conditions of one bar atmospheric pressure, about 25°C, an excess of free water (below the water table) and commonly a 'high' oxidation potential due to equilibration with atmospheric oxygen. Under these conditions major alteration reactions occur. Many minerals become unstable, due to oxidation (for example, of Fe^{2+} and S_2^{2-} in pyrite to Fe^{3+} and SO_4^{2-}) or hydration. Water movement across the mineral surfaces during weathering provides the medium for the provision of aqueous species to a reaction and for carrying away any soluble reaction products. In particular, gold could become mobilized during supergene alteration by a number of mechanisms:

- (i) oxidation and dissolution of gold and silver from native gold, especially of low fineness (section 6), due to the higher level of dissolved oxygen in the weathering zone;
- (ii) release of gold during mineral weathering (i.e. of gold telluride or gold disseminated in pyrite). This gold may be fine grained and therefore reactive;
- (iii) mechanical abrasion of native gold by collapse or swelling of minerals during alteration, resulting in release of gold as a colloid or sol;
- (iv) increased concentration of ligand molecules such as chloride, sulfide or thiosulfate, resulting in higher gold solubility.

Clearly the solubility of gold is dependant not only on such gross properties as system Eh, but also on weathering of other minerals, particularly pyrites, as discussed below.

3.2 Thermodynamic and Kinetic Controls

As a background to a discussion of sulfide oxidation and weathering (section 3.3), a distinction should be made between thermodynamic and kinetic controls of a chemical reaction. Thermodynamic theory determines how a system should change: specifically it shall alter so as to minimize the Gibbs Free Energy (G°) of the system. Thus, the oxidation of pyrite (FeS_2) to ferrous iron (Fe^{2+}) and sulfate (SO_4^{2-}):



will generally be highly thermodynamically favoured where the solution is equilibrated with atmospheric oxygen. However, reactions of this type, though thermodynamically favourable, may occur at very slow rates due to a kinetic barrier to the reaction. This is shown in Fig. 1.

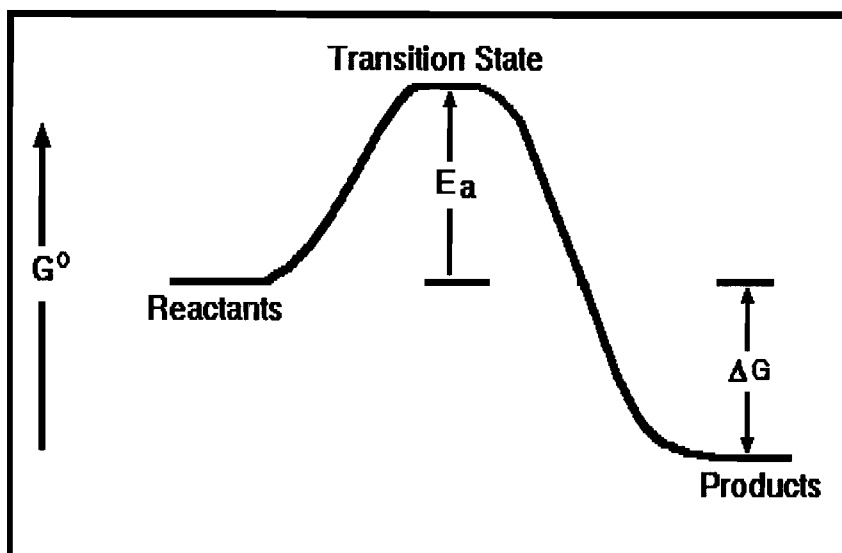


Figure 1: Diagrammatic Representation of a Chemical Reaction.

If a reaction is exothermic, i.e. has a negative ΔG , then the reaction is thermodynamically favourable. Note, however, that in order to complete the reaction the reacting species must go through (at least) one transition state of high energy. The energy that must be gained to reach this transition state is known as the activation energy (E_a). Where the activation energy is high then the reaction rate may become very slow. Thus, ΔG determines whether a reaction is favourable, and E_a determines the rate. This is demonstrated in Fig 2 which shows the diagrammatic reaction pathways for two reactions: Reaction A has a high ΔG (thermodynamically highly favourable) and a high E_a (slow reaction rate); while Reaction B has a low ΔG (less thermodynamically favourable) and a low E_a (high reaction rate).

3.3 Pyrite Weathering

Early work on pyrite weathering and heavy metal mobilization (Garrels, 1954; Garrels and Naeser, 1958) indicated that the only sulfur anions expected to be of any significance were sulfide and sulfate, based on thermodynamic considerations. However, more recent work has found pyrite weathering to be complicated by kinetic factors, as discussed below.

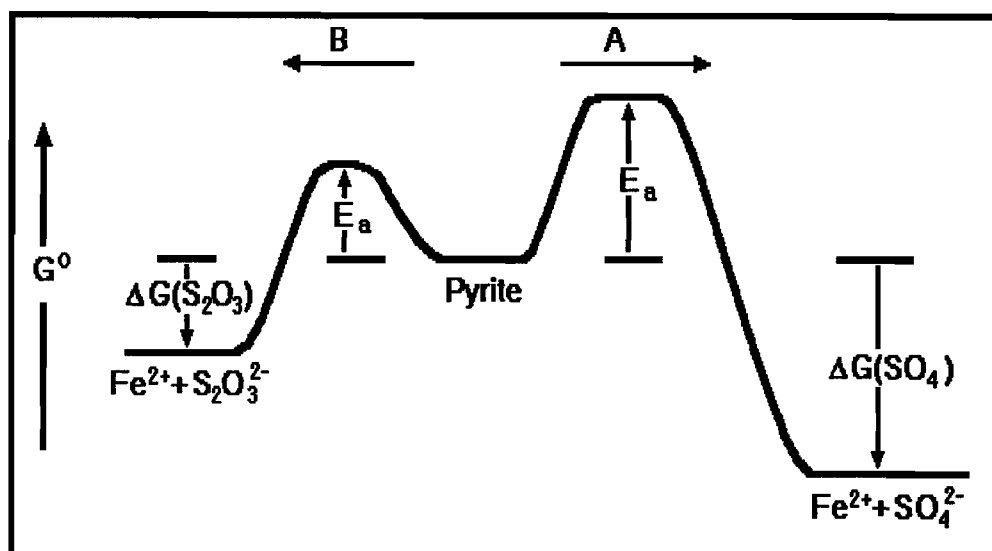


Figure 2: Two Potential Pathways for Oxidation of Pyrite in Neutral and Alkaline Conditions.

There are two reaction pathways of major importance in pyrite oxidation: (A) oxidation of pyrite to sulfate in acid solution (Eqn. 1 above); and (B) oxidation of pyrite to thiosulfate ($\text{S}_2\text{O}_3^{2-}$) in neutral to alkaline solution:



During acid oxidation of pyrite the sulfur is generally completely oxidized to sulfate. Pyrite oxidation releases protons (Eqn. 1) and can therefore create acidic conditions. Thus, acid oxidation and therefore sulfate production during pyrite weathering is common. However, if the pyrite is 'buffered' by the presence of carbonates then protons released by pyrite oxidation are absorbed by the carbonates:



and conditions will remain neutral to alkaline during oxidation. Two of the thermodynamic and kinetic pathways under these conditions are represented in Fig. 2.

Complete oxidation of pyrite to sulfate (reaction A) occurs very slowly, due its high E_a , but partial oxidation of the pyrite to thiosulfate (reaction B) is favoured due to a lower E_a of this reaction. Therefore, 'meta-stable' species such as thiosulfate and sulfite (SO_3^{2-}) which have a lower activation energy for formation may be found in solution during pyrite weathering despite the fact that $-\Delta G$ for their formation from pyrite oxidation is less than that for sulfate. Thus, even though thiosulfate and sulfite concentrations, on thermodynamic grounds, should not exceed 10^{-6} moles/litre (M) under equilibrium conditions, and therefore should have little geochemical significance (Garrels, 1954; Garrels and Naeser, 1958) a number of workers (Listova *et al.*, 1966; Granger and Warren, 1969) have observed appreciable concentrations of these species during oxidation of sulfides. These observations are supported by laboratory observations (Goldhaber, 1983; Webster, 1984) demonstrating that thiosulfate is the major sulfur species produced by pyrite oxidation where the pH is above 7.5. The thiosulfate so produced is, in the absence of bacteria,

highly stable: for example, thiosulfate solutions at pH 7 were aerated for 4 months under sterile conditions with less than 10% change in concentration (Rolla and Chakrabarti, 1982).

The hypothesis of long-lived meta-stable species is further supported by Subzhiyeva and Volkov (1982) who determined the following concentrations of various thio species in thermal and hydrothermal waters:

Sulfide (S^{2-}):	16 - 450 mg/L	(mean 170)
Sulfate (SO_4^{2-}):	60 - 6800 mg/L	(mean 1500)
Thiosulfate ($S_2O_3^{2-}$):	0.4 - 15 mg/L	(mean 2.2)
Sulfite (SO_3^{2-}):	0.08 - 9 mg/L	(mean 1.0)

Significant levels of thiosulfate and sulfite were observed. Sulfide concentration was also high. The sulfate:sulfide ratio varied between 1 and 100. This would suggest that the redox potentials (section 3.4) of the solutions analysed were all within the range -0.235 and -0.205 V at pH = 7. It is highly unlikely that all of the waters analysed are so similar in Eh; instead it is suggested that, in addition to thiosulfate and sulfite, sulfide is also not in equilibrium with sulfate. Thus, thiosulfate, sulfite and possibly sulfide exist in solution in the oxidized zone in levels above those calculated for thermodynamic equilibrium.

3.4 Influences of Eh and pH on Gold Solubility

Thermodynamic and kinetic factors are affected by solution properties such as pH, redox potential (Eh) and ionic strength. pH is the negative logarithm of the hydrogen ion activity (aH^+ ; approximately equals the ion concentration ¹); for every decrease in pH of one unit there is a ten-fold increase in hydrogen ion concentration. Thus, if a reaction requires protons then decreasing the pH will thermodynamically favour the reaction.

As shown in Eqn. 1, complete oxidation of the pyrite releases protons and decreases pH. Any gold dissolution reactions that require protons would be favoured thermodynamically during pyrite weathering.

For pyrite to weather it must be in contact with an aqueous solution rich in oxygen (high redox potential). The redox potential of a reaction (Eh^0 value) refers to a case where all gases are at one atmosphere and all dissolved substances are at an activity of one mole per 1000 grams of water (approximately 1 M). Eh^0 values have been determined experimentally for a large number of oxidation reactions, in the form of 'half-reactions'. Thus, the half-reaction for the oxidation of native gold to Au^{3+} (auric ion) in water is



¹ Solution activities are generally closely related to concentrations and in most instances any errors will cancel out in calculations. In this report all activities are equated to concentrations.

This reaction will be 'coupled' with another half-reaction that occurs at a higher E_h° . However, the E_h° of this reaction is so high (i.e. gold is so difficult to oxidize) that water itself will be oxidized to oxygen first:



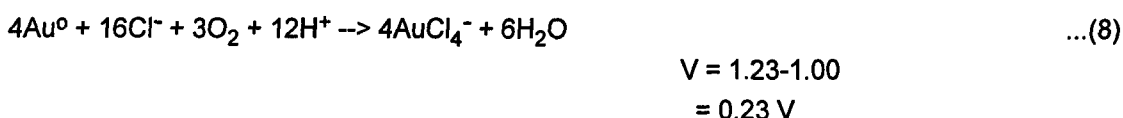
As the E_h° of gold oxidation is higher than that of water oxidation, then Au^{3+} (if formed) could oxidize water:



Thus, the 'naked' gold cation Au^{3+} never reaches significant levels in water. Observable levels of gold in solution occur due to other molecules and ions (*e.g.* chloride, hydroxide) which act to complex the gold ion and render the oxidation reaction more thermodynamically favourable. The stronger the complex the greater the reduction in E_h° . A ligand such as chloride will lower the E_h° for oxidation of gold metal from 1.50 to 1.00 V:



The E_h° of gold oxidation is now lower than that of water oxidation (Eqn. 5). Thus, oxygen can oxidize gold in the presence of chloride:



The gold(I) cyanide species (aurous cyanide) is a very strong complex and the E_h° of oxidation of Au^0 to Au^+ is reduced from 1.68 in pure water to -0.59 V in the presence of one mole/litre (1 M) cyanide:



This complex will therefore have a high stability even in reducing (low oxygen) solutions, assuming that cyanide is present in solution at significant levels.

The E_h° values given above are, as described earlier, for a standard state where all solutes are at one M concentrations. However, we are more interested in the solution potentials (E_h values) where gold will be just soluble. This was chosen to be where gold concentration equals 10^{-6} M (0.2 mg/L) as this possibly represents a level in solution where significant gold mobility could occur. The E_h values where the particular gold complex is soluble at 10^{-6} M will be less than the E_h° of the complex: by 0.35 V for Au(I) complexes; and by 0.12 V for Au(III) complexes. Conversely if the concentration of the ligand ion is reduced (note that naturally occurring solutions seldom have ions present at concentrations of one M or more) then the E_h for solubility of gold is increased. These factors should be borne in mind in any discussion of reduction/oxidation reactions. In general, where an E_h for gold solubility is given in this report then it corresponds to the E_h for a gold solubility of 10^{-6} M, and for the particular ligand concentrations given in the text. Thus, for example, the E_h for solution of 10^{-6} M $\text{Au}(\text{CN})_2^-$, where CN^-

concentration equals 10^{-5} M (0.26 mg/L), is calculated ² to be -0.349 V. Details for such calculations are given in Appendix 1.

The type of data discussed above is often presented in the form of an Eh-pH diagram, as shown in Fig. 3, which graphically represents the dominant gold species in pure water.

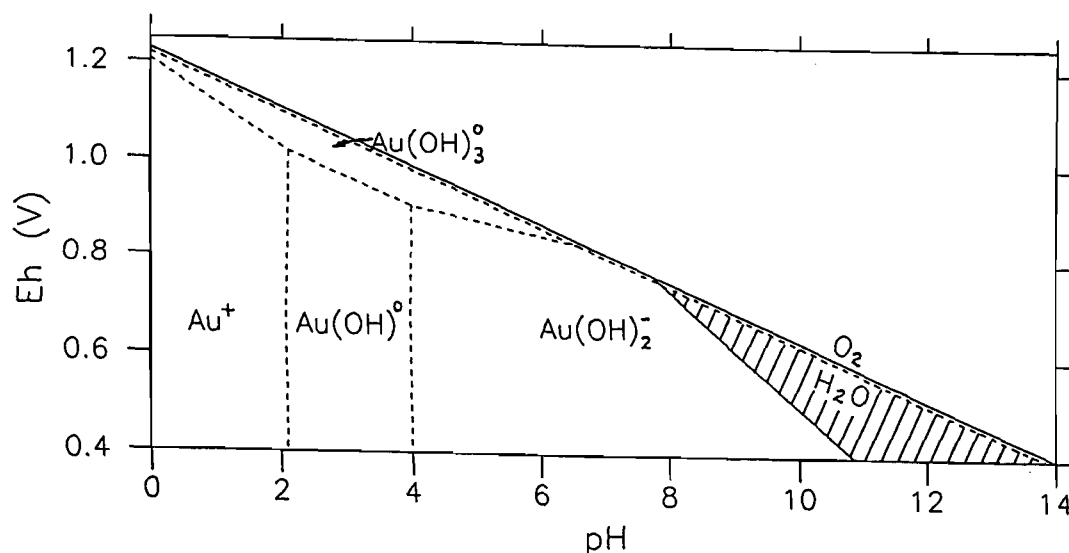


Figure 3: Eh-pH Stability Diagram for the System Au-O₂-H₂O at 25°C and 1 atm.
Gold concentration contours are given for equilibration with gold metal.

As can be observed, four gold species are dominant in pure water under various Eh/pH conditions: Au⁺, Au(OH)[°], Au(OH)₂⁻ and Au(OH)₃[°]. The hatched area indicates the zone over which gold solubility ([Au]) is greater than 10^{-6} M . Thus, gold has appreciable solubility only in water of pH > 8 under oxidized conditions (see section 4.2).

Gold solubility is likely to be highly dependant on environmental factors such as concentration of solutes, Eh and pH. These factors may change in a number of different ways. Workers have delineated the various Eh-pH regimes expected under various conditions, based on observed Eh/pH data (Baas Becking *et al.*, 1960) and on the predicted controlling reactions (Sato, 1960). The data of Sato (1960) is summarized in Fig. 4.

As the system moves from depth, there is a major increase in Eh and, in many instances, a major increase in acidity, both of which will tend to increase gold solubility.

² Unless otherwise stated all thermodynamic calculations were performed by the author, either manually or using the U.S.G.S. speciation program PHREEQE (Parkhurst *et al.*, 1980).

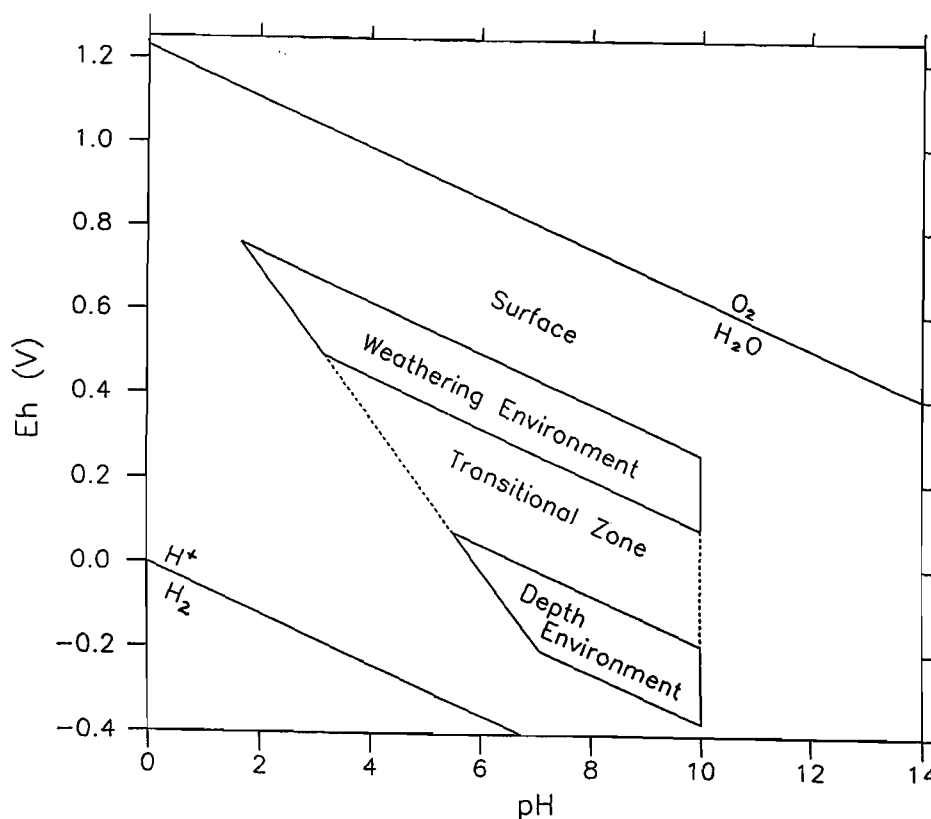


Figure 4: The probable ranges of Eh-pH for both the weathering environment and the depth environment. (modified from Sato, 1960).

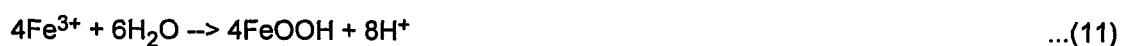
Figure 4: The probable ranges of Eh-pH for both the weathering environment and the depth environment. (modified from Sato, 1960).

3.5 Near-Surface Processes / Ferrollysis

Solutions close to the surface may become particularly corrosive. All the alkali and alkaline earth metals are leached out, leaving a residue of (predominantly) iron, aluminium and silicon. One potential source of acidity is ferrollysis (Brinkman, 1977). As ferrous iron is exposed to highly oxidizing conditions near the surface, it is oxidized to ferric iron:



Ferric iron in solution is hydrolysed and precipitated:



This precipitation reaction releases protons. Such reactions can reduce pH to below 3 in iron-rich groundwaters (Sato, 1960; Mann, 1984a) and mobilize heavy metals (Mann, 1983). Acid/oxidizing solutions are (in the presence of chloride) an important environment for gold mobilization (section 4.3).

4. FACTORS LEADING TO GOLD DISSOLUTION

4.1 General Overview of Gold and Silver Solubilities

Calculated redox potentials of some gold and silver complexes which may be significant in the natural system are given in Table 2. A full list of the critical thermodynamic constants are given in Appendix A. The individual complexes will be described later in greater detail and Table 2 is only a general overview of gold and silver chemistries.

Table 2: Comparative E_h^0 values of gold and silver complexes with geochemically important ligands. (calculated from Webster, 1985).

Ligand	Gold		Silver	
	Complex	E_h^0 (V)	Complex	E_h^0 (V)
	Au^+	1.68	Ag^+	0.80
	Au_3^+	1.5	-	-
Cl^-	$AuCl_4^-$	1.00	$AgCl_4^{3-}$	0.44
HS^-	$Au(HS)_2^-$	-0.08		
$S_2O_3^{2-}$	$Au(S_2O_3)_2^{3-}$	0.14	$Ag(S_2O_3)_2^{3-}$	0.00
SO_3^{2-}	$Au(SO_3)_2^{3-}$	0.32	$Ag(SO_3)_2^{3-}$	0.29
CN^-	$Au(CN)_2^-$	-0.59	$Ag(CN)_2^-$	-0.38
SCN^-	$Au(SCN)_2^-$	0.20	$Ag(SCN)_2^-$	0.30

Gold has two oxidation states - Au(I) and Au(III) - whereas silver only occurs in solution as Ag(I). Gold in the absence of any complexing molecules is very insoluble whereas silver, with an E_h^0 of 0.8 V, has a significant solubility even in pure water. The silver halide complexes (represented here by $AgCl_4^{3-}$) have redox potentials below the E_h values commonly found in the weathering environment (Sato, 1960), suggesting a high solubility. However, silver solubility may still be limited by precipitation of silver chloride (section 4.3).

The thio-complexes of gold [$Au(HS)_2^-$, $Au(S_2O_3)_2^{3-}$, $Au(SO_3)_2^{3-}$] have E_h^0 values only slightly above those of the corresponding silver complexes (Table 2). Thus, it is possible that in zones where pyrite is weathering under neutral to alkaline conditions (section 3.3) silver and gold will have similar mobilities.

The E_h^0 values of the gold cyanide (CN^-) and thiocyanate (SCN^-) complexes are very low. Thus, gold mobility may be high in environments containing soluble cyanide (or thiocyanate). Such environments may exist in profiles where these ions have been generated by biological activity (section 4.6).

The geochemistries of gold and silver are highly dependant on the weathering environment and the concentration of various solutes. This will be expanded upon in sections 4.2 to 4.11.

4.2 Hydrolysis Complexes of Gold and Silver in Water

The gold species observed in water are as shown in Fig. 3. Using the available thermodynamic data gold appears to have substantial solubility under alkaline ($\text{pH} > 8$) oxygenated conditions, due to the high stability of the $\text{Au}(\text{OH})_2^-$ complex (Baranova and Ryzhenko, 1981). (Note that the author is not aware of any work outside of the Soviet Union substantiating the importance of this complex). The $\text{Au}(\text{OH})_2^-$ complex will also be of importance when other salts are present. Calculations by the author indicate that water equilibrated with calcite and gypsum may have a pH of up to 9.1, depending on other ions present. *i.e.* under these conditions gold will have a solubility above 10^{-6} M if the solution is equilibrated with atmospheric oxygen.

Silver is much more readily oxidized than gold and has appreciable solubility in oxygenated water. Silver has a solubility (as Ag^+) of 10^{-5} M (1 mg/L) at pH values up to 11 and a Eh of 0.50 V, indicating a high mobility of silver even in the absence of other ligands.

Percolating solutions of water with low concentrations of complexing anions will only occur in areas of high rainfall and good drainage systems, such as a sandy soil with a low organic component. As these solutions will also be equilibrated with atmospheric CO_2 , they will be neutral to acid. Under these conditions gold will be geochemically immobile whereas silver should be ultimately leached out of the system, leading to partition of these metals. However, if alkaline conditions prevail then gold may also have a significant mobility.

4.3 Chloride and Other Halide Complexes

Chloride has long been suspected of being an important ligand for gold. The first detailed thermodynamic investigation on gold chloride complexes was performed by Krauskopf (1951), who showed that appreciable gold (greater than 10^{-6} M or 0.2 mg/L) may be solubilized as AuCl_4^- in the presence of a strong oxidizing agent such as MnO_2 or O_2 when the pH is less than 3 and chloride ion concentration is greater than 10^{-3} M (40 mg/L). Cloke and Kelly (1964) stated that if an activity of 10^{-5} M Au is chosen then gold is soluble for solutions of $\text{pH} < 5.5$, $\text{Eh} > 0.9$ V and $[\text{Cl}^-] > 10^{-3.2}$ M (20 mg/L). At first sight such conditions should be similar to those in many natural waters. In fact, this statement does not make clear that pH must be at most 5.5, and that where Eh is just 0.9 V then $[\text{Cl}^-]$ must be above 10^{-1} M; *i.e.* highly acid, saline conditions are required, with high redox potentials. The only solid phase studied by these and other workers (Miller and Fisher, 1973) able to generate such a high Eh in solution was pyrolusite (MnO_2). The relevant half-reaction is



from which, if the $\text{Mn}^{2+}/\text{MnO}_2$ couple is controlling the solution Eh, the solution redox potential can be determined from

$$\text{Eh} = 1.23 - 0.030 \log[\text{Mn}^{2+}] - 0.118 \text{ pH} \quad \dots(13)$$

The situation where the solution Eh/pH is controlled by the $\text{Mn}^{2+}/\text{MnO}_2$ couple is simulated in Fig. 5 for $[\text{AuCl}_4^-]$ equals 10^{-6} M, $[\text{Mn}^{2+}]$ equals 10^{-5} M (0.6 mg/L), and $[\text{Cl}^-]$ equals 10^{-1} M (3500 mg/L). The Mn concentration used in Fig. 5 represents what is expected to be a reasonable lower level at which

Mn could be controlling Eh/pH, and the chloride concentration represents saline conditions. As can be observed, the range over which MnO_2 can oxidize Au^0 (stipled area) is limited to low pH (< 4) and high Eh (> 1 V) values. Such solutions represent environments that are virtually fully equilibrated with atmospheric oxygen (represented by the dashed line). The area over which oxygen can oxidize gold (the hatched area in Fig. 5) includes less severe pH values (up to about 5).

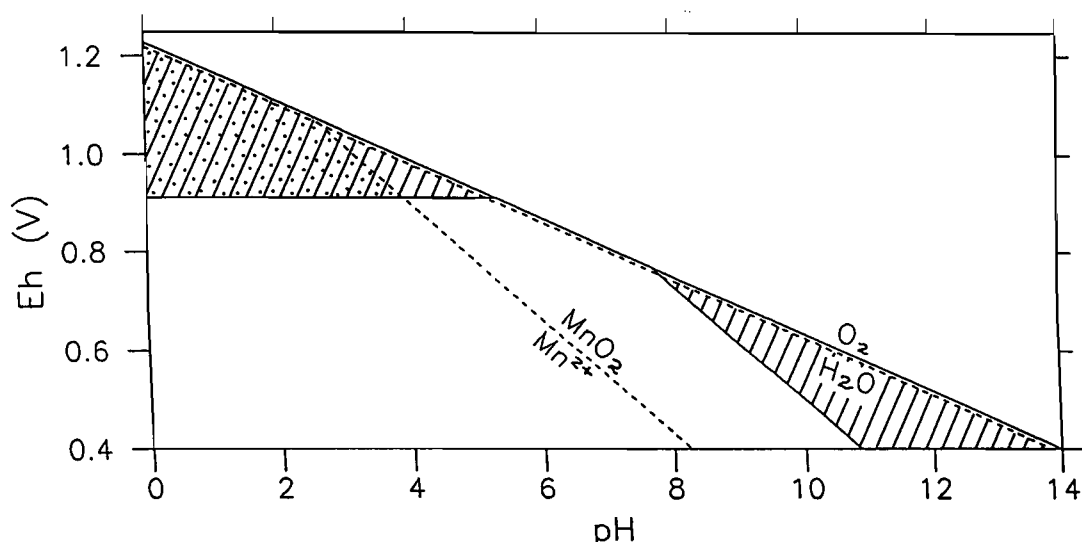


Figure 5: Eh-pH Stability Diagram for the System Au-Cl-MnO₂-O₂-H₂O, for [Au] equals 10⁻⁶ M, [Mn²⁺] equals 10⁻⁵ M, and [Cl⁻] equals 10⁻¹ M.

Following from this, and utilizing the more exhaustive thermodynamic database now available (Smith and Martell, 1976; Wagman *et al.*, 1982) the Eh-pH stability diagram for the Au-Cl-O₂-H₂O system is represented in Fig. 6.

As can be observed from Fig. 6, the gold chloride complex which defines gold solubility at [Cl⁻] = 10⁻¹ M is AuCl₂⁻, rather than AuCl₄⁻ as generally assumed. For chloride levels at and above 10^{-2.3} M the AuCl₂⁻ complex is soluble at 10⁻⁶ M under less oxidizing conditions than AuCl₄⁻ (see Appendix C for details). This would suggest that the solubility of gold chloride has previously been slightly underestimated. Nevertheless the general conclusions remain substantially unchanged. Gold is soluble (*i.e.* [Au] > 10⁻⁶ M) in highly oxidized saline solution, though only over a very limited pH range: 0-5.5 for [Cl] = 10⁻¹ M (3500 mg/L); and 0-3 for [Cl] = 10⁻² M (350 mg/L). Decreasing the chloride concentration from 10⁻¹ to 10⁻² M increased the Eh for gold oxidation from 0.91 to 1.01 V. Thus, in this example the stabilities of AuCl₂⁻ and AuCl₄⁻ in solution is a complex interplay of Eh, pH and chloride concentration.

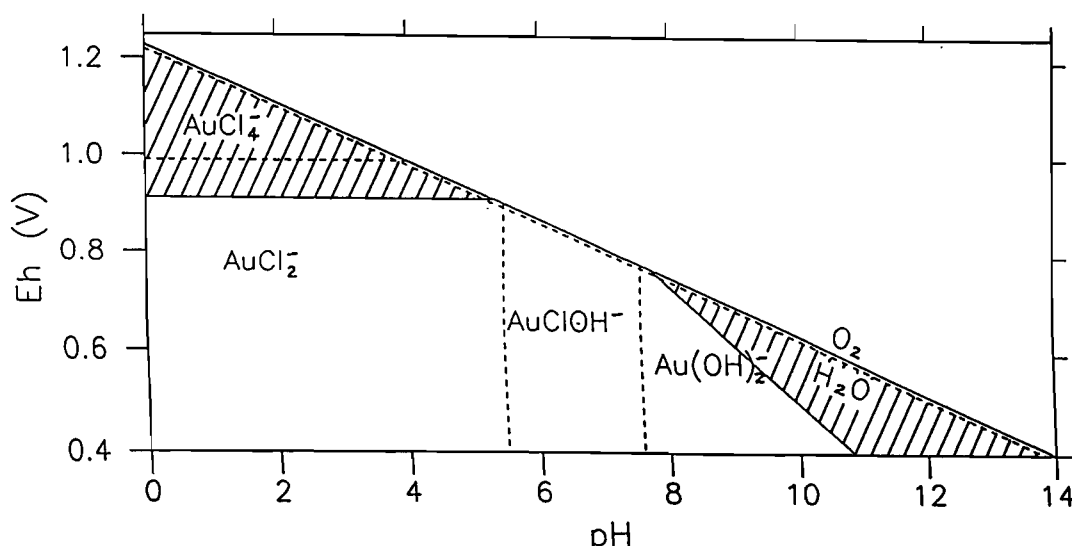


Figure 6: Eh-pH Stability Diagram for the System Au-Cl-O₂-H₂O at 25°C and 1 atm, with [Cl] = 10⁻¹ M, equilibrated with gold metal.

The other halides form stronger complexes than chloride, as demonstrated by their redox potentials:



However, because of their low concentrations relative to chloride the other gold halides generally make a minor contribution to gold and silver solubility (Boyle, 1979; Webster, 1985). They could be of significance where the weathering parent material included minerals containing bromine or iodine (e.g. bromargyrite) or if weathering or biological processes acted to concentrate bromide or iodide, relative to chloride.

As discussed above and indicated in Table 2, chloride is a relatively weak ligand for gold. However, it is of potential geochemical importance due to the occurrence of saline waters associated with gold deposits and the stability of chloride to precipitation or decomposition, relative to other ligands listed in Table 2. This is discussed further in section 8.5.

Data for silver (Appendix A) indicates the Ag/AgCl₄³⁻, Ag/AgCl₃²⁻ and the Ag/AgCl₂⁻ couples have Eh⁰ values less than 0.5 V. Thus, at Eh⁰ values above 0.5 V solubility is defined, not by the oxidation potential of silver metal but by the solubility of cerargyrite (AgCl; Webster, 1985) and the stability constants of the various silver-chloride complexes. Results for total silver solubility for chloride solutions are given in Table 3 (see also Appendix D).

Silver has a solubility in pure water at Eh of 0.5 V of 10⁻⁵ M (0.35 mg/L; Appendix D) and this increases for more oxidizing conditions. Thus, silver solubility is reduced to below 10⁻⁵ M (0.04 mg/L) over the chloride concentration range 10⁻⁴ to 10⁻¹ M, relative to a higher silver solubility in chloride free water.

Table 3: Silver solubility vs chloride concentration in moderately oxidized ($E_h > 0.5$ V) solutions.

[Cl] (M)	Total [Ag]	
	(M)	(mg/L)
10^{-4}	$10^{-5.7}$	0.071
10^{-3}	$10^{-6.4}$	0.014
10^{-2}	$10^{-6.3}$	0.019
10^{-1}	$10^{-5.4}$	0.15
10^0	$10^{-3.5}$	12.3

In summary, gold is solubilized in chloride solution. However, the solutions need to be saline, acidic, and equilibrated with atmospheric oxygen to allow significant gold mobilization. Such conditions are much more likely close to the weathering surface than at depth. Thus, specific groundwater or soil water conditions are required to ensure gold chloride mobilization, whereas silver is mobile in many weathering regimes, often leading to partitioning of the two metals.

4.4 Sulfide Complexes

The interaction of gold with sulfide solution has been widely studied, though much of this work has been involved in investigating the potential of gold sulfide complexes in hydrothermal deposition (e.g. Seward, 1973, 1982; Boyle, 1979; Baranova and Ryzhenko, 1981). However, such complexes may also be of importance in the supergene zone. Sulfide may commonly exist in solution at 10 - 1000 mg/L in the vicinity of pyrite deposits (section 3.3). The optimum conditions for $\text{Au}(\text{HS})_2^-$ dissolution occur at about $E_h = -0.12$ V and $\text{pH} = 7$. Under more oxidizing conditions sulfide will be oxidized. Assuming a total dissolved sulfur content of 2×10^{-2} M then total dissolved gold under these conditions will equal 6×10^{-6} M. Such reducing conditions (required to ensure sulfide is not oxidized) are generally not found in the supergene and weathering zone. Under highly reducing conditions ($E_h < -0.1$ V; generally caused by organic matter) and neutral pH, bacteria are able to reduce sulfate to sulfide (Zobell and Rittenberg, 1948; Wheatland, 1954), which could solubilize gold. This contrasts with gold chloride complexes where mobility is limited by gold reduction. Thus, gold sulfide complexes are of importance in quite different weathering zones from gold chloride complexes.

4.5 Thiosulfate and Sulfite complexes

Thiosulfate and sulfite, the meta-stable products of pyrite oxidation (section 3.3), are probably of greater importance to gold dissolution in the weathering zone than sulfide, due to their greater (meta-) stability. The gold complexes with these anions are generally moderately stable under alkaline, neutral and slightly acid conditions though they are quickly decomposed under acid conditions (Boyle, 1979). It is difficult to accurately determine the solution stabilities of these complexes as they are presumably dependent on the presence or absence of factors that could catalyse breakdown of the thiosulfate or sulfite. Such factors could include low pH, biological organisms, organic matter, variable oxidation state metals such as Fe or Mn, or adsorptive surfaces.

A number of workers (Listova *et al.*, 1966; Goleva *et al.*, 1970; Lakin *et al.*, 1974; Pitul'ko, 1976; Plyusnin *et al.*, 1981; Webster, 1984, 1986; Webster and Mann, 1984) have pointed to the importance of these complexes, especially in circumstances where buffering of the primary pyrite by carbonates has led to oxidizing solutions remaining neutral to alkaline (section 3.3). Mann (1984b) has calculated that 400-800 g of CaCO_3 is required for every 240 g of FeS_2 in order to maintain alkaline conditions for thiosulfate production. Thus, there will be significant gold thiosulfate mobilization only where the carbonate: pyrite ratio is at or above this level.

Stoffregen (1986) suggests that gold and silver in the oxidized zone of an ore body has been transported via thiosulfate complexes during acid weathering of pyrite. However, the evidence for this is weak, as the carbonate content of the original material is not given. Thus, though conditions are now acid the initial parent material may have contained significant carbonate. Stoffregen (1986) also found very high silver levels near the top of the unoxidized zone. High levels of silver in solution that would result from weathering of these minerals could explain the anomalously high silver (> 2 %) observed in some of the secondary gold. Additionally, there could be localized mobilization due to a small area of the deposit where carbonate was anomalously high.

Investigations by Webster (1984, 1985, 1986) suggest that as well as gold and silver thiosulfate complexes having similar chemistries the two metals may be complexed together in the presence of thiosulfate in a mixed $(\text{Au,Ag})(\text{S}_2\text{O}_3)_2^{3-}$ complex. Such a complex could be dissolved directly from electrum, and gold and silver would then be precipitated together when the complex was decomposed. Webster (1986) considers that such a mixed $(\text{Au,Ag})(\text{S}_2\text{O}_3)_2^{3-}$ complex could explain observations of ore deposits at sites like Wau, in Papua New Guinea, where secondary gold has a high silver content, unlike other sites where secondary gold has a very high fineness. However, this phenomena could also be explained by the similar chemistries of the two separate thiosulfate complexes. Note that secondary gold in equilibrium with $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ will be 985 fine, and secondary gold in equilibrium with $\text{Au}(\text{SO}_3)_2^{3-}$ and $\text{Ag}(\text{SO}_3)_2^{3-}$ will be 770 fine (see section 6 for details). Secondary gold appears to form via adsorption or decomposition of the $\text{S}_2\text{O}_3^{2-}$ or SO_3^{2-} ligands, rather than by the reduction mechanism; however, this study suggests that secondary gold formed from thio complexes could contain high silver.

4.6 Cyanide and Thiocyanate Complexes

Gold forms a very strong $\text{Au}(\text{CN})_2^-$ complex, which is stable over a wide range of pH/Eh conditions (Fig. 7). The limiting factor to gold-cyanide solubility is available cyanide concentration. Thus, to maintain a concentration of 10^{-6} M (0.2 mg/L) gold the solution must contain at least $2 \times 10^{-6} \text{ M}$ (0.032 mg/L) cyanide. Certain plants and micro-organisms are known to release cyanide (Lakin *et al.*, 1974; Sneath, 1972). Bacteria such as the cyanogenic species *Chromobacterium violaceum* produce up to 200 mg/L cyanide *in vivo* (Rodgers and Knowles, 1978), and can solubilize up to 215 mg/L (10^{-3} M) gold from the pure metal (Smith and Hunt, 1985). Cyanogenic bacteria are frequently associated with plants, soil and organic matter (Corpe, 1951; Saupe *et al.*, 1982) and zones such as a highly organic horizon or the immediate surroundings of an active root of a cyanogenic plant (Knowles, 1976) could contain elevated levels of cyanide and give rise to mobile gold. Such gold could be absorbed by the plant (Shacklette *et al.*, 1970; Girling *et al.*, 1979; Warren, 1982) or other organisms, leading to accumulation in the organic litter, or could be mobilized, giving rise to leaching of gold from soil.

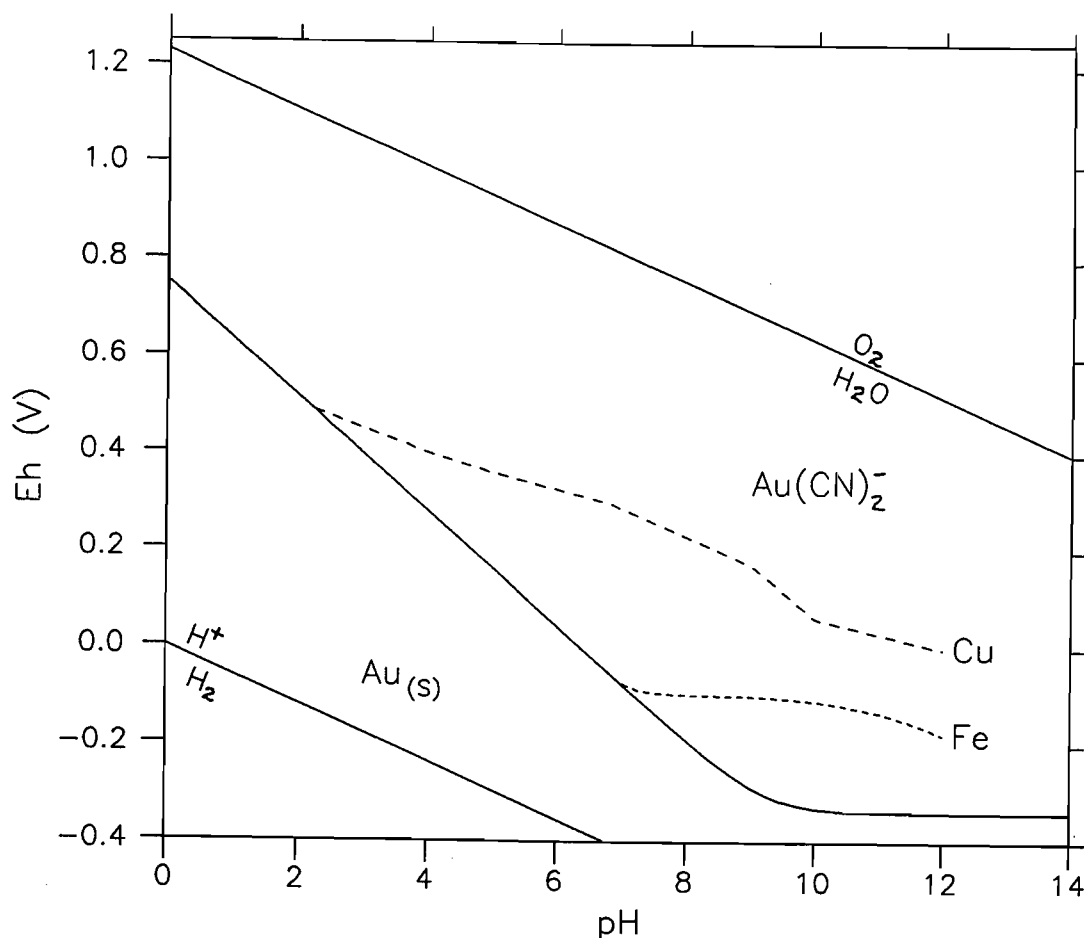


Figure 7: Eh-pH Stability Diagram for the system Au-CN-O₂-H₂O, at 25°C and 1 atm, for [Au] equals 10⁻⁶ M and [CN⁻] equals 10⁻⁵ M. The solid, fine dashed, and coarse dashed lines represent the lower limit for Au solubility: in the absence of any interfering cations; in the presence of 1 M Fe; and where [Cu] is determined by the solubility of the least soluble Cu solid at that Eh-pH regime.

Cyanide has a very high affinity for gold, and generally other metals such as iron interfere with gold-cyanide formation only weakly. Thus, the presence of 1 M Fe²⁺ only increases the Eh for dissolution of 10⁻⁶ M gold in 10⁻⁵ M (0.26 mg/L) cyanide solution from -0.34 V to -0.10 V (Fig. 7), which still indicates Au(CN)₂⁻ to be highly soluble. The only metal likely to interfere significantly with gold dissolution by cyanide is copper. This is indicated in Fig. 7. The upper dashed line shows the Eh for gold dissolution as Au(CN)₂⁻ where Cu solubility is controlled by the various Cu minerals. This second approach may roughly simulate the situation where both Au and Cu are present in a soil solution influenced by cyanide. Over the pH range 4 - 9 the Eh for gold dissolution varies between 0.4 and 0.17 V. The Au(CN)₂⁻ complex is inert in moderately acid, neutral and alkaline conditions (Boyle, 1979). However, as with the gold thiosulfate complex, decomposition of the cyanide and precipitation of the gold may occur as the result of specific chemical or biological factors.

Thiocyanate is a product of biological activity and of the chemical alteration of cyanide. The gold and silver thiocyanate complexes [Au(SCN)₂⁻, Ag(SCN)₂⁻] are weaker than the cyanide complexes (Table 2) and would therefore be less readily formed and more easily decomposed.

4.7 Organic Matter Interactions

Organic matter is known to be important in the dissolution of heavy metals, even in the presence of significant excesses of major cations (Reuter and Perdue, 1977; Hering and Morel, 1988). In general, the Group IB elements (copper, silver and gold) are strongly bound by humus (Boyle, 1968, 1977). In view of this, a number of workers have investigated gold - organic matter interactions. The results from these investigations have varied and are detailed below.

Some of the earliest work on gold - organic matter interactions was done by Freise (1931), who found that organic matter extracted from lignite was able to take gold into solution in the absence of oxygen. Additionally, water from a stream high in organic matter was able to mobilize gold in an artificial soil. In comparison, Fetzer (1934, 1946) found that dissolved organic matter from his sources, derived in a similar manner to Freise (1931), did not dissolve gold, but instead precipitated solutions of auric chloride *in vivo*, presumably via reduction of the gold. The most likely explanation for this is differences in the material that each worker extracted. Thus, for example, Freise's (1931) material could have been composed of organic acids with more complexing groups (e.g. carboxylate and sulfide groups) and less reducing groups (e.g. phenolic groups) than the organic material used by Fetzer (1934).

Work by Ong and Swanson (1969) was in basic agreement with that of Fetzer (1934). They also found that organic acids could not solubilize native gold, but instead were able to reduce auric chloride to Au^0 . The Au^0 did not precipitate but instead formed a colloidal suspension which was stabilized by the organic acids. This gold colloid was highly stable (up to 8 months) and could represent a significant mechanism for gold mobilization.

Baker (1973, 1978) found that solutions of 500 mg/L humic acids extracted from a podzolic soil were able to dissolve $1.0 - 1.7 \times 10^{-6} \text{ M}$ (0.2 - 0.3 mg/L) Au under oxidizing conditions (pH = 3.5, Eh = 0.33 V). Results indicated that the gold existed in a complexed, rather than a colloidal, form. Solvent extraction suggested that the Au-humate complex is stronger than the Au-chloride complex and of similar stability to the Au-SCN complex.

Similar results were also found by Boyle *et al.* (1975) who dissolved up to $0.8 \times 10^{-6} \text{ M}$ (0.15 mg/L) Au with 5000 mg/L humic acid. The resulting gold colloid (see section 4.9) was greater than 50 μm in size. Varshal *et al.* (1984) found that solutions of 30 mg/L fulvic acid could solubilize 0.1 and $1.3 \times 10^{-6} \text{ M}$ (0.02 and 0.3 mg/L) Au at pH 3.5 and 7.5 respectively.

Conversely Fedoseyeva *et al.* (1986) found that their humic and fulvic acid preparations, in solution concentrations of $4 \times 10^{-5} \text{ M}$ at pH 4.5 - 4.9, were able to reduce AuCl_4^- and AuBr_4^- , but not complexes of lower Eh° [e.g. AuI_2^- , Au(urea)_2^+ and $\text{Au(S}_2\text{O}_3)_2^{3-}$]. This gives an Eh for oxidation of the organic acids in these experiments between 0.7 and 1.1 V.

Part of the explanation for the variable reactions between organic matter is due to differences between various organic materials. Thus, solid lignite, which is a highly reduced form of organic material, would be expected to primarily act as a reductant, whereas soluble humic acids in oxidized solution could conceivably act as a complexing agent for Au(I) or Au(III). As well, reaction conditions are probably of major importance. Where auric chloride concentration equals 10^{-2} M dissolved humic acid primarily acts as a reductant, bringing the gold solution level to an equilibrium level of, say, 10^{-6} M . Conversely if the

same soluble humic acid were to be equilibrated with gold metal in an oxidized solution, it could act as a complexing agent, and bring soluble gold up to an equilibrium level of 10^{-6} M. Thus, though the net result is much the same, the former experiment would characterize organic matter as a reducing agent, whilst the latter experiment would characterize organic matter as a complexing agent.

In conclusion, organic matter may possibly be an important control on both the mobilization and deposition of gold. Boyle (1979) writes "An important question in the transport of gold is not whether gold can be bound by humic materials - this much seems proved - but whether it can migrate in natural solutions in this manner". Further work is certainly required to detail the important gold - organic matter interactions in the natural system.

4.8 Micro-organisms and Plants

As described in sections 4.6 and 4.7, biologically derived species such as cyanides, thiocyanates and organic matter may be of importance in solubilizing gold. A number of workers (Razin and Rozhkov, 1966; Shacklette *et al.*, 1970; Kaspar *et al.*, 1972; Girling *et al.*, 1979; Warren, 1982; Smith and Keele, 1984; Erdman and Olson, 1985) have demonstrated that many plants can accumulate or adsorb gold, and may represent a useful exploration medium. The mechanism for this is not clear, though certainly a number of compounds secreted by plants (cyanide, thiocyanate, amines, organic acids) are very effective in complexing gold. Quite possibly mechanisms which accumulate copper and other essential elements may also take up gold as well. Some plants not only accumulate gold but may be important in its redistribution, taking up gold at depth and then depositing it at the surface as leaf litter (Erdman and Olson, 1985). This hypothesis may explain some zones of depletion and concentration close to the surface (*ibid.*).

In addition to plants and plant products, bacteria and other micro-organisms may have significant effects on gold solubility and may be of use in gold exploration (Watterson, 1985). Bacteria commonly alter the surrounding chemistry by catalysing reactions: thus, (for example), sulfur bacteria may cause gold solubility by initiating pyrite oxidation or reduce soluble gold by catalysing thiosulfate breakdown (Postgate, 1951). Certain species of bacteria may release or decompose cyanide (Knowles, 1976; Rodgers and Knowles, 1978; Smith and Hunt, 1985), which will have major effects on gold solubility (section 4.6); while other bacteria could cause significant gold solubility as amino acid complexes (Korobushkina *et al.*, 1974).

4.9 Gold as a Colloid or Sol

Gold readily forms colloids or sols (*i.e.* molecular aggregations up to 5 μ m in size) and such species have been known for centuries (Boyle, 1979). The formation of colloids or sols via reduction of dissolved gold with organic matter and the stability of these resultant suspensions has been demonstrated by a number of workers (Goni *et al.*, 1967; Ong and Swanson, 1969; Ong *et al.*, 1970; Fedoseyeva *et al.*, 1986), and colloidal gold stabilized by organic matter has been postulated as an important mechanism for the mobilisation of gold. These colloids are negatively charged and therefore would be mobile in negatively charged soils, precipitating where they contact a soil horizon with positively charged minerals such as iron oxides. Colloidal gold has not been observed in the natural environment, either by Boyle (1979) using dialysis methods or by Kolotov *et al.* (1980) using filtration techniques. However, this lack of evidence is

not surprising, given the low gold content of most waters and the difficulty in obtaining groundwater samples with changing solution conditions [e.g. Eh, pH, dissolved gas concentrations (CO_2 or H_2S)]. Thus, though gold colloids could be significant for gold mobility there is as yet no positive evidence for the existence of colloidal gold in natural solutions.

4.10 Arsenate, Tellurate, Antimonite, etc.

These ligands have been suggested by Boyle (1979) as possibly important in gold mobility due to the expected high stability of the particular gold complexes, and the fact that these elements are often observed associated with gold. Ligands containing these elements would be expected to significantly effect gold solubility where the element required is present in high levels in weathering minerals (e.g. antimony in stibnite) - as may occur in a number of gold deposits. Unfortunately little, if any, substantial work on the chemistry of gold with these potential ligands has been done. Investigation in this area is considered necessary to further elucidate the potential importance of arsenic, tellurium and antimony in gold mobility and as pathfinder elements.

4.11 Conclusion

The potentially important complexes that could raise the solubility of gold to 10^{-6} M or greater are summarized in Table 4.

The Eh/pH conditions under which thermodynamically stable complexes of gold (not including cyanide or organic matter) are soluble at or above 10^{-6} M, for optimized conditions (i.e. $[\text{Cl}] = 10^{-1}$ M, $[\text{S}] = 10^{-1}$ M) are shown as the hatched zones in Fig. 8. The areas of gold solubility are limited to extremely reducing $[\text{Au}(\text{HS})_2^-]$ or highly oxidizing $[\text{AuCl}_4^-]$, $[\text{Au}(\text{OH})_2^-]$ conditions. Under certain weathering conditions thiosulfate can increase gold solubility. However, it seems that it is the biologically generated ligands (cyanide, organic acids) that will be of most significance in gold mobilization in many environments. Such questions as: how much cyanide does a plant root secrete; how does the reducing/complexing behaviour of organic matter change with aging or percolation down a profile, etc. are of critical importance. Further work in this area may yield important data for an understanding of gold mobilization in the weathering profile.

Table 4: Potentially Important Aqueous Gold Species.

Species	Possible Origin	Solubility Range
$\text{Au}(\text{OH})_2^-$	Oxidative dissolution of gold under alkaline conditions.	oxidized pH>8
$\text{AuCl}_2^-/\text{AuCl}_4^-$	Oxidative dissolution of gold under acid/saline conditions.	oxidized/saline/acidic <i>i.e.</i> pH<5.5 Cl>10 ⁻¹ M or pH<2 Cl>10 ⁻³ M
$\text{Au}(\text{HS})_2^-$	Dissolution of gold by reduced waters during early supergene alteration, or by reducing solutions generated by biological action.	reduced/neutral Eh < -0.1V pH 6 - 9 totalsulfur > 0.02 M
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$	Weathering of gold/pyrite in neutral to alkaline solution.	alkaline to weakly acid (meta-stable)
$\text{Au}(\text{CN})_2^-$	Interaction of cyanide with gold.	limited by cyanide content
Au - organic matter	Interaction of organic matter with gold under oxidizing conditions.	Not certain, may depend on source of material Eh>0.4V(?)
Colloidal gold	May be formed during reduction of gold by organic matter.	Presence not confirmed for natural waters

5. FACTORS LEADING TO GOLD PRECIPITATION

It is commonly observed that gold mobilization generally occurs only over short distances. Therefore, effective mechanisms must exist to remove gold from solution. These mechanisms can be either solution based or dependent on mineral phases present, and may result in a large number of secondary gold morphologies.

5.1 Changes in Solution Chemistry

Given the low solubility of gold under most solution conditions (Fig. 8), reprecipitation readily occurs when conditions change. Thus, $\text{Au}(\text{OH})_2^-$ is precipitated as the pH falls or conditions become less oxidizing, the gold-chloride complexes are precipitated by reduction in Eh, rise in pH, or even by simple dilution, $\text{Au}(\text{HS})_2^-$ is precipitated by rise in Eh above -0.1 V, and meta-stable thio complexes of gold are irreversibly decomposed by acid waters. Such changes in solution properties occur due to evaporation, mixing with other groundwaters, or effects of moving into soil horizons containing minerals which react with the soil solution.

The dependence of gold solubility on solution properties may explain why secondary gold precipitates may be observed with no distinct association with secondary minerals (Lawrance, 1988). Conditions suitable for gold dissolution may occur only over very short flow lengths, giving rise to several generations of dissolution and reprecipitation in a very short distance. Major redistribution of gold over the time-scale of rock weathering could require more severe dissolution conditions or via small movements over an extended timespan.

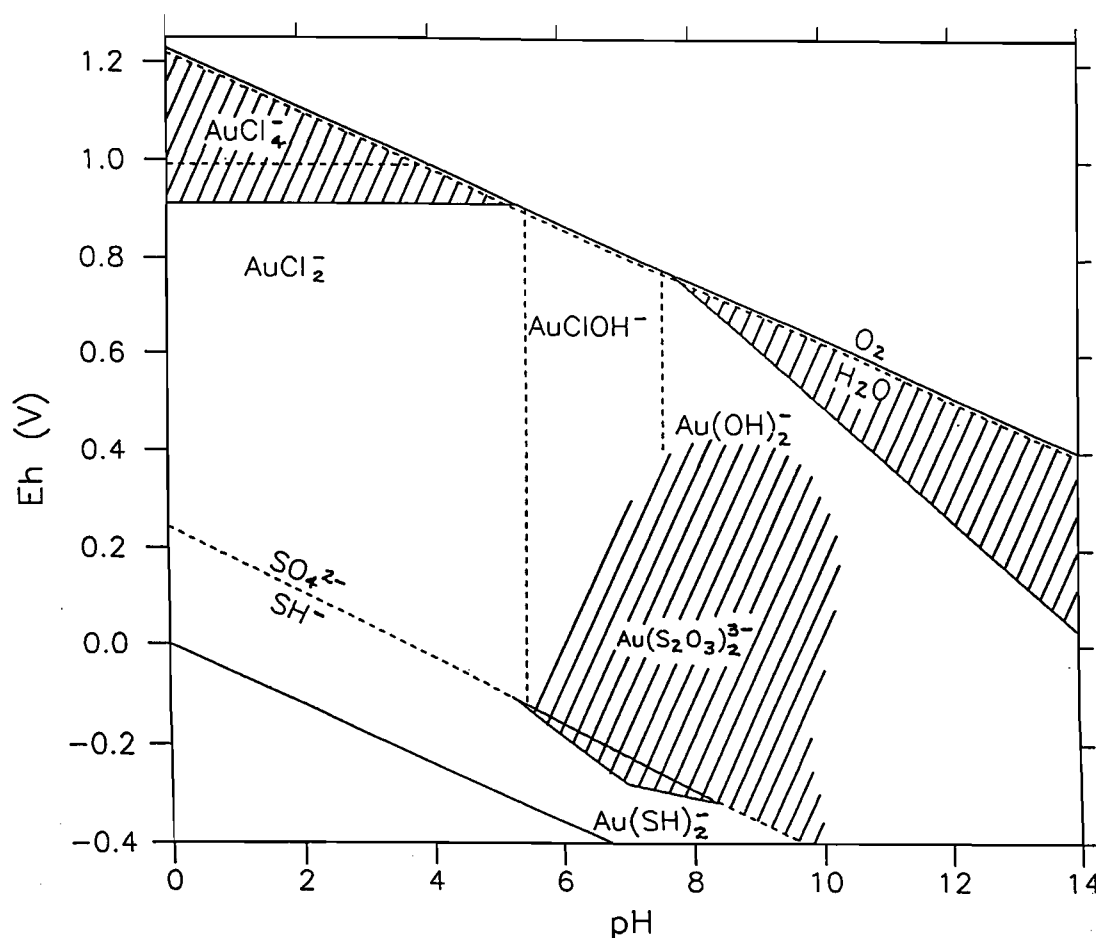
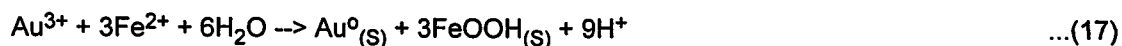


Figure 8: Eh-pH Stability Diagram for the System Au-Cl-S-O₂-H₂O at 25°C and 1 atm, with [S] = 10⁻¹ M, [Cl] = 10⁻¹ M, equilibrated with gold metal.

5.2 Reactions with Metal Ions

Meta-stable ligands such as thiosulfate and sulfite may be important for gold mobilization under some weathering regimes. Metals ions such as Fe, Mn and Cu can catalyse breakdown of these ligands (Conklin and Hoffmann, 1988). Thus, the presence of iron in solution or of precipitated goethite may act to quickly precipitate gold-thio complexes.

Mann (1984b) suggests that Fe²⁺ in solution will be effective in precipitating gold viz



while leaving silver, with its lower redox potential, in solution. Such reactions are also important as they can act as co-precipitation mechanisms, possibly resulting in the intimate mixing of native gold with iron oxides.

5.3 Reactions with Natural Materials

Most natural materials are able to precipitate gold from its solutions, via reduction, co-precipitation and adsorption or colloidal coagulation (Boyle, 1979 and references given therein). The most effective materials appear to be the sulfides, arsenides, tellurides, sulfosalts, native metals including gold, calcite, clay minerals, finely divided chlorite, graphite, carbon, pyrite, and sapropel. The ease of removal of gold complexes is generally in the order



Gold, being a heavy metal, is readily adsorbed by various mineral phases such as iron oxides. Work by Nechaev (1984) showed that the gold-chloride complexes are readily adsorbed by hematite, up to the ppm level. Adsorption and coprecipitation mechanisms (Eqn. 17) may explain the commonly observed association of gold with the iron oxide phases (Foster et al., 1978; Evans, 1981; Crone et al., 1984; Mann, 1984a,b; Smith and Keele, 1984; Wilson, 1984; Freyssinet et al., 1987). The usefulness of As as a pathfinder element may also be a function of the correlation of As with iron oxides (Koons, et al., 1980; Gray, 1986). These two mechanisms seem of particular importance for the gold halides and other weak complexes. Other, more stable, complexes, such as $\text{Au(S}_2\text{O}_3)_2^{3-}$ (Fedoseyeva and Strel'tsova, 1987) and possibly Au(CN)_2^- are less strongly adsorbed and may be highly mobile.

As discussed in section 4.7, organic matter, particularly in solid form, may be a very effective precipitant for gold. Thus, workers such as Gatellier and Disnar (1988) have been able to readily form crystalline gold by reacting auric chloride with solid organic matter. Fedoseyeva et al. (1986) found that the adsorption coefficient (defined as the ratio of the adsorbed species per unit weight adsorbate to the dissolved species per unit volume) of soluble gold complexes on humus was strongly correlated to the E_h of the complex. This suggests that adsorption occurs either by reduction of the gold and/or by dissociation of the complex. The net result is that weak complexes of gold (e.g. AuCl_4^-) will be readily adsorbed by organic material whereas strong complexes of gold [e.g. $\text{Au(S}_2\text{O}_3)_2^{3-}$, Au(CN)_2^-] will be only weakly adsorbed.

Gold may also co-exist with solid organic matter in ionic or fine colloidal form. Grégoire (1985) found that most of the gold in stream sediments and in two B horizon samples were extractable in hypochlorite, which dissolves organic matter but would not be expected to be an effective extractant for gold metal nuggets. This indicates a major proportion of the gold in these samples was associated with organic materials, or in a finely divided form. Similarly Roslyakov (1984) found that gold in soils was predominantly found in insoluble mineral residues or in fulvic acid complexes.

5.4 Decomposition of Ligand Molecules

As discussed above, some of the most stable gold complexes [Au(HS)_2^- , $\text{Au(S}_2\text{O}_3)_2^{3-}$, Au(CN)_2^-] are limited by the stability of the ligand ions. Thus, Au(HS)_2^- is unstable to oxidation above -0.1 V, though it may be observed under more oxidizing conditions as a meta-stable species. $\text{Au(S}_2\text{O}_3)_2^{3-}$ is meta-stable and is readily decomposed by acid conditions. Au(CN)_2^- is potentially of high stability. The most important cause of decomposition is possibly bacterial. However, complexed cyanides can commonly travel 50 - 100 m with little reduction in concentration, suggesting that the gold-cyanide complex could be very important for gold mobility.

5.5 Changes in Surface Charge of Soils

The mobility of mobile gold species, particularly gold colloids, may be dependant on the surface charge of soils. A negatively charged colloid may have a high mobility in soils predominantly containing clay minerals with negative charges. However, if this colloid is transported into a zone containing sesquioxides (iron and aluminium oxides), which have positive charges under mildly acid conditions, the colloidal gold is highly likely to precipitate. Such a mechanism is a possible explanation for zones of gold concentration in laterite (see section 8.3) or bauxite.

5.6 Conclusion

Given the low solubility of gold, it is not surprising that gold is readily reprecipitated. Gold may be precipitated just by changes in solution characteristics such as Eh, pH, concentration or salinity. The observation of gold precipitating in pores independent of the surrounding minerals is therefore entirely sensible.

Various solid phases and dissolved ions can also initiate gold precipitation, either by reducing, adsorbing or co-precipitating with the gold or by providing a surface for decomposition of meta-stable ligands. Organic matter may be particularly important for the adsorption of gold from solution.

6. FINENESS OF SECONDARY GOLD IN THE SUPERGENE ZONE

Primary gold generally contains appreciable silver (> 5%) and is considerably more soluble than pure gold (Mann 1984a,b; Webster 1984, 1986). This is due largely to the much higher solubility of silver, relative to gold. Secondary gold is commonly of higher fineness than its primary source (Boyle, 1979; Wilson, 1984). Thus, there is an observed tendency during weathering to go from alloyed gold/silver towards pure gold metal. This could be achieved either by dissolution of the electrum, followed by gold metal precipitation or via leaching of the silver from the electrum.

If the conversion of electrum to pure gold occurs by silver leaching then thermodynamic studies on this process will require an estimate of the silver activity in the electrum. Fig. 9 shows the activity of gold and silver vs the fineness of electrum (data for this figure is given in Table B1).

The information in Fig. 9 can be considered a correction of the data for silver activity in electrum given by Stoffregen (1985). Therefore, for electrum 810 fine the silver activity is 0.1, rather than unity. Thus, in any calculations for dissolution of silver from 810 fine electrum the activity of the solid silver used is 0.1, rather than one as for dissolution from silver metal. Therefore, the Eh for leaching of this silver from 810 fine electrum will be increased by 0.059 V, relative to that for dissolution of pure silver (see Appendix B for calculations). However, even though the silver in the electrum is less soluble than pure silver, it is still highly soluble relative to gold. It is calculated that in a chloride solution gold metal would have to be of the order of 999.99999998 fine (*i.e.* virtually pure gold) for the silver to be as insoluble as the gold.

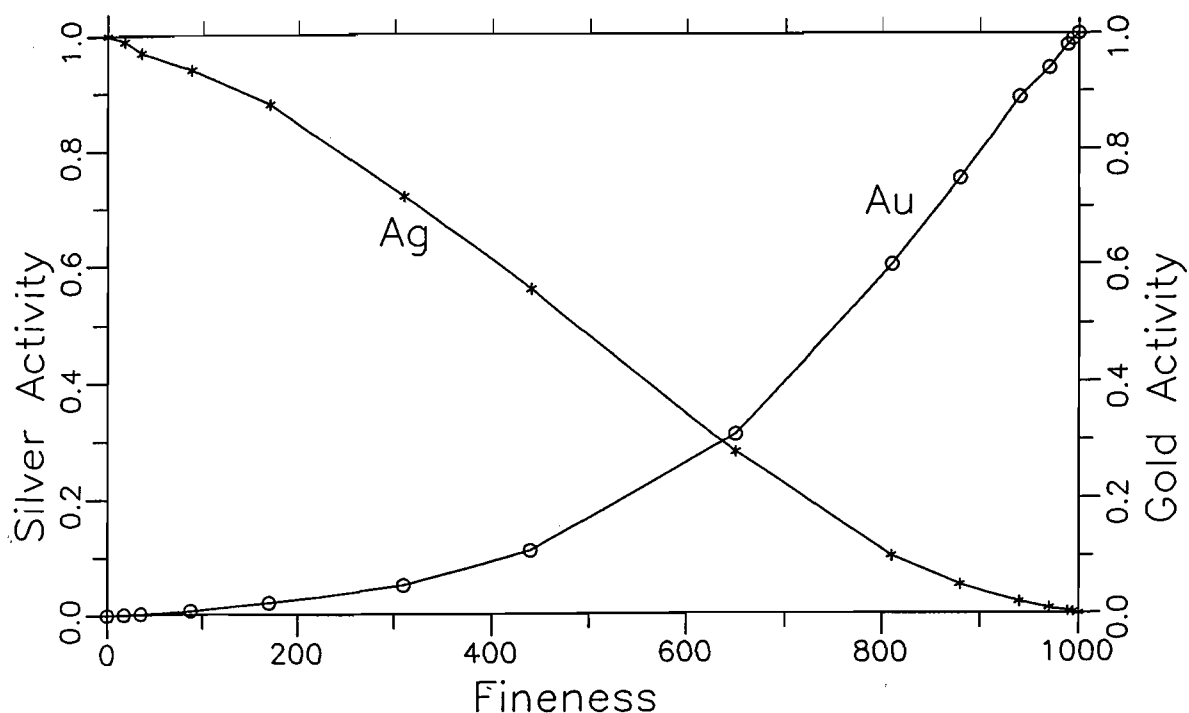


Figure 9: Gold and Silver Activities vs Fineness for Electrum (see Appendix B for details).

Similar calculations for the other important gold ligands (Appendix B) indicates that the equilibrium fineness of gold is dependent on the gold complex controlling solubility. This is shown in Table 5.

Table 5: Equilibrium Electrum Composition for Various Ligands.

Ion	Final Electrum Composition	
	mole% Ag	fineness
Cl ⁻	5 x 10 ⁻⁹	1000
Br ⁻	1 x 10 ⁻⁸	1000
I ⁻	2 x 10 ⁻⁸	1000
SH ⁻	0.3	998
S ₂ O ₃ ²⁻	2.6	985
SO ₃ ²⁻	35	770
SCN ⁻	90	170
OH ⁻	99	17
CN ⁻	99.7	5

As shown, the trend towards pure gold during weathering is most marked for the halide complexes and sulfide, weaker for thiosulfate and sulfite and reversed for thiocyanate, hydroxide and cyanide. Thus, in speaking of the trend towards pure gold during weathering one should consider which complexes are controlling gold and silver solubility, as this determines the equilibrium silver content.

Mann (1984b) indicated the trend towards pure gold for chloride solutions graphically, and his figure is redrawn in this report as Fig. 10.

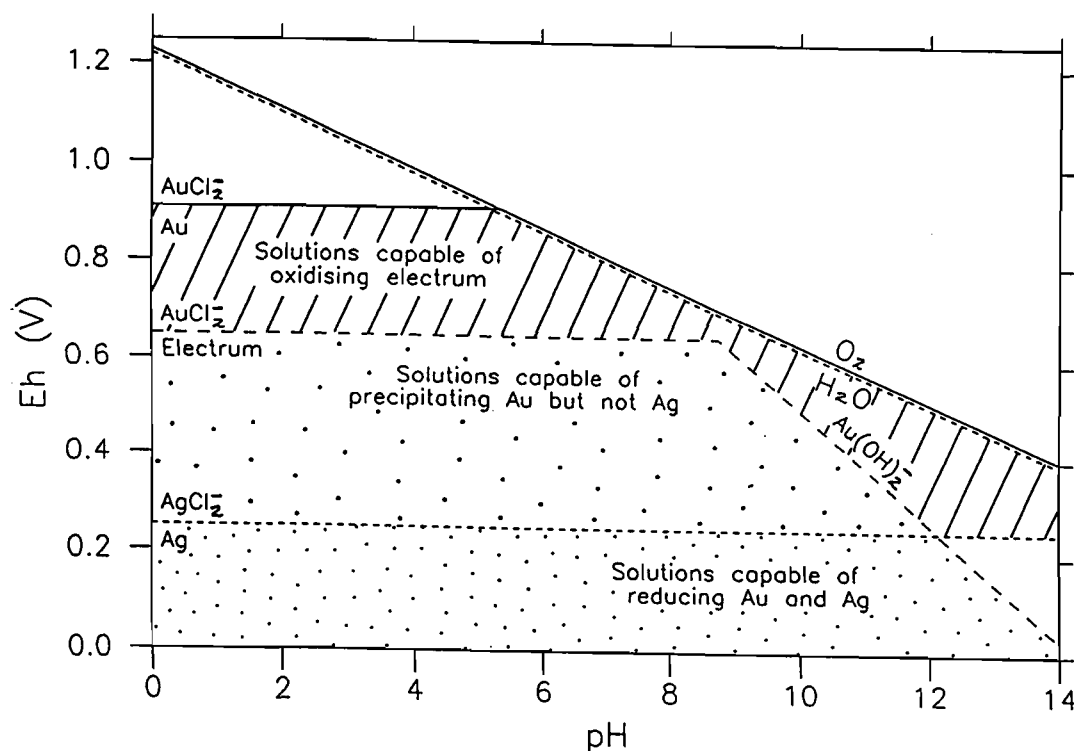


Figure 10: Eh-pH Stability Diagram for gold, silver and an Au/Ag alloy (electrum; modified from Mann, 1984b).

As can be seen, electrum is more readily dissolved than gold metal, being dissolved at an Eh of about 0.6 V. However, at this Eh the dissolved gold chloride complex is unstable relative to gold metal. Thus, ions in solutions such as Fe^{2+} will reduce the gold and a separate phase of high fineness gold metal will be formed. Silver, which is of higher stability in solution than gold, will remain in solution and be leached from the system.

Exceptions to the rule of formation of higher fineness gold during weathering appear to occur where thiosulfate is present (Webster 1984, 1986, Webster and Mann, 1985) and gold and silver reprecipitate together. This precipitation may be caused by manganese oxides, which occur in appreciable quantities at the site investigated by Webster. The oxides could precipitate the thiosulfate by co-precipitation (section 5.2), adsorption (section 5.3) or by catalysed decomposition of the thiosulfate ion (section 5.4). This hypothesis (of low fineness secondary gold occurring where gold and silver were mobilized as the thiosulfate complexes) is consistent with the lower equilibrium fineness of gold equilibrated with gold and silver thiosulfate and/or sulfite (Table 5).

7. ALTERATION OF PRIMARY METALLIC GOLD

Primary gold is commonly observed as a resistate mineral in the weathering environment, though often in altered form. The nature of this alteration may also provide clues as to the weathering mechanisms that have occurred in the profile and may assist in exploration.

7.1 Increased Fineness

Where primary gold grains survive into the upper part of the weathered zone they may be of higher fineness than gold in the unweathered rock (Hallbauer and Utter, 1977; Freyssinet and Butt, 1988a,b). This is consistent with the expected composition of gold metal equilibrated with weathering solutions (section 6). Two possible mechanisms for this effect are:

- (i) selective dissolution of Ag-rich gold grains, leaving a residual of Ag-poor grains;
- (ii) selective leaching of silver from electrum, resulting in the grains having reduced silver contents.

At present, the relative importance of these two mechanisms has not been determined. Leaching of silver [mechanism (ii)] would not be expected to be fast enough to reduce the silver contents of whole grains significantly during weathering. Many grains and small nuggets have Ag-poor rims (see section 7.3), resulting in increased fineness. The increase in fineness of primary gold during weathering is postulated to be due to selective dissolution of Ag-rich grains and formation of Ag-poor rims. These two mechanisms may be distinguishable using transmitted electron microscope studies of the Ag-poor rim (section 7.3). Both processes could occur simultaneously in the profile.

7.2 Dissolution/Etching

Gold grains are commonly observed to be etched or partially dissolved (Mann 1984a; Freyssinet *et al.*, 1987; Freyssinet and Butt, 1988a,b,c; Lawrance, 1988). Iron oxides are sometimes observed associated with etched surfaces, and the observed morphologies suggest that there has been partial replacement of gold by iron oxide (Mann, 1984a). Small particles of high fineness gold within the iron oxides have presumably precipitated from the solubilized primary gold.

Etched surfaces may also show secondary precipitation, suggesting several generations of dissolution and precipitation over a scale of a few μm (Lawrance, 1988). Such observations are consistent with the ease of precipitation of gold (section 5).

7.3 Formation of Silver-Poor Rims

Silver-poor rims have commonly been observed on the surface of primary gold grains in weathered profiles and in placer deposits (Desborough, 1970; Desborough *et al.*, 1970; Koshman and Yugay, 1972; Czamanske *et al.*, 1973; Nefedov *et al.*, 1982; Mann, 1984a; Giusti and Smith, 1984; Giusti, 1986; Michel, 1987; Freyssinet *et al.*, 1987; Bowles, 1988; Freyssinet and Butt, 1988b,c). These rims are solid and can

be clearly distinguished from "lacy" rims that possibly result from direct precipitation of gold from solution (Giusti, 1986). The Ag-poor rims consistently have the following properties:

- (i) the rims generally contain $< 1\%$ Ag, in comparison with the grain interior with $> 5\%$ Ag;
- (ii) the rims are generally of the order of $50\text{ }\mu\text{m}$ thick, and commonly are of irregular shape;
- (iii) the interface between the low silver rim and the interior is very sharp, with gradients of $0.5 - 7\%$ Ag/ μm (and possibly even higher, as this measurement is affected by the resolution of the electron microprobe beam of about one μm);
- (iv) variations in the Ag content of the primary grain do not influence the composition of the rim;
- (v) copper is depleted in the same way as silver;
- (vi) in some instances morphological and mineralogical aspects suggest that the phenomenon is due to Ag leaching rather than gold dissolution;
- (vii) low silver rims have been observed in cracks within the gold grains.

Points (i) to (v) suggest that the process must be one of gold solution and deposition. However, points (vi) and (vii) are more consistent with silver leaching, at least on the macro scale. A possible explanation, here termed galvanic silver loss, is described below.

We have previously discussed (section 6) how electrum is of higher solubility than gold under many circumstances. The consequence of this is that gold and silver will be dissolved from electrum and then gold reprecipitated as pure gold metal, as postulated by Mann (1984b). Some of the reaction steps for such a reaction could include:

- (i) diffusion of oxidizing species to the electrum surface;
- (ii) the redox reaction of this species at the surface;
- (iii) combination of the ionized gold with a reducing species in solution;
- (iv) the second redox reaction of gold with the reducing species.

Though dissolution of gold from electrum and reprecipitation elsewhere as pure gold may be thermodynamically favourable, there are a number of kinetic barriers for such a mechanism, as suggested above. A more kinetically favourable mechanism would be to short-circuit this mechanism via an electrum/gold galvanic cell, as represented in Fig. 11.

By this process Ag and Au are released as ions. The electrons released are retained within the grain and flow to another, nearby, part of the grain where gold plating occurs. Here the electrons reduce the incoming gold ions to a plate of high purity gold. By this mechanism the number of reaction steps and kinetic barriers to the formation of high fineness secondary gold are significantly reduced.

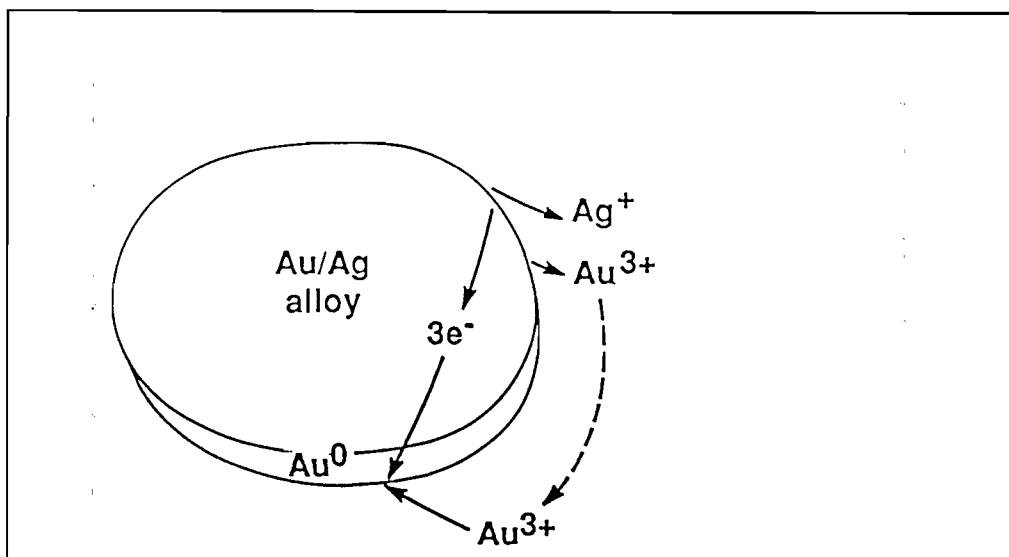


Figure 11: Diagrammatic Representation of Formation of Ag-Poor Rims by Galvanic Silver Leaching.

The macro-analogue of this electrum/Au cell was indicated by Mann and Webster (Mann, 1984a; Webster, 1984, 1986) when they demonstrated that significant Voltages could be generated between electrum and gold metal under a variety of solution conditions. The favourability of such a reaction is demonstrated by the ubiquitous nature of Ag-poor rims of this type.

Silver-poor rims can cover part or all of the primary grain (Giusti, 1986). Mann(1984a) described gold grains in which on one side dissolution of gold is occurring or has occurred at an interface with iron oxide whilst a Ag-poor rim is observed on the other side of the grain. It is also conceivable that for small grains (*i.e.* less than 100 μm diameter) the generation of Ag-poor rims could actually replace all of the electrum grain with pure gold.

If the Ag-poor rim progresses to the stage where it totally covers the grain then it may act to preserve its primary structure, and even high silver grains may be preserved in the weathering profile, as have occasionally been observed (Freysinet and Butt, 1988b).

8. ENVIRONMENTS OF GOLD REDISTRIBUTION

8.1 General Overview

Having discussed the solution chemistry of gold and silver in aqueous solution it is now possible to predict the chemical behaviour of these metals in the natural environment. In the following sections, various natural environments are described where gold mobilization is predicted to occur. Where possible these environments are listed in terms of their order in a weathering sequence. The reader is referred to other work on profile development (Butt and Smith, 1980; Butt, 1987) for details on the development of profiles under differing conditions. The ultimate aim of an analysis of gold mobility in various environments is to

gain a sense of the sequence of gold dissolution, precipitation and alteration processes that would have occurred during particular weathering and landscape development processes.

8.2 Sulfide Weathering Front

Weathering of sulfides and its effects on gold solubility were extensively discussed in sections 3.3, 4.4 and 4.5. In general, weathering solutions need to be neutral to alkaline in order to stabilize $\text{Au}(\text{HS})_2^-$ in reducing conditions and $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ in weakly oxidizing conditions. Such pH conditions can occur due to the presence of carbonates, if present at or above concentrations of 400-800 g of CaCO_3 for every 240 g of FeS_2 (section 4.5). Under more acid conditions these complexes will not form and hence gold will not be mobilized.

Gold mobility during sulfide weathering as the chloride complex was suggested by Cloke and Kelly (1964) who found that the reaction of 1 M sulfuric acid and 1 M sodium chloride with either goethite (FeOOH) or pyrolusite (MnO_2) created solution conditions that etched native gold. It was suggested that similar conditions would be found where the alteration of pyrite deposits was occurring during alternate wetting and drying; however, studies of sulfide weathering (Garrels and Naeser, 1958; Sato, 1960) suggest that solutions in contact with weathering pyrite would seldom, if ever, match the particular solution conditions described above (i.e. high acidity, high chloride, $E_h > 0.9 \text{ V}$). In the absence of further evidence, it is suggested that gold chloride mobilization during supergene alteration of pyrite is unlikely.

8.3 Lateritic Horizons

Several authors have pointed to lateritic zones as important in gold redistribution (Evans, 1981; Mann 1984b; Freyssinet *et al.*, 1987), and indeed gold is often found intimately associated with iron oxides in many profiles (Foster *et al.*, 1978; Crone *et al.*, 1984; Mann, 1984a; Smith and Keele, 1984; Wilson, 1983, 1984). The chemical reason for this is not certain; however, the redox reaction of Fe^{2+} with dissolved gold (Eqn. 17) does result in precipitation of both metals. Additionally, near the surface of lateritic zones oxidation of Fe^{2+} can cause highly acid conditions (ferrolysis; section 3.5), which can destabilize thiosulfate and other ligands, resulting in precipitation of the complexed gold. Iron oxide strongly adsorbs gold from solution (Nechaev, 1984) and the adsorbed gold could ultimately be recrystallized as gold metal. Also, iron has a variable oxidation state and could have a major role in catalysing breakdown of meta-stable and supersaturated gold complexes.

Iron oxide rich profiles have the additional property of possessing positively charged surfaces, whereas more clay rich zones will have negatively charged surfaces. Thus, gold species such as negatively charged colloids, which will be mobile in the clay zone, will have a lower stability in the iron oxide zone. This hypothesized phenomenon would also result in gold precipitation in lateritic zones.

All of these mechanisms could potentially cause a strong association between gold metal and iron oxides. Thus, it is postulated that iron oxides can act as a gold sink, both during and subsequent to large scale laterization.

8.4 Upper Soil Horizons

The upper soil horizons may be an important zone for gold mobilization. Possible contributors to gold mobilization are:

- (i) gold chloride complexes in saline, acid, oxidizing conditions (uncommon);
- (ii) thio complexes generated by bacterial reduction of sulfate (high organic matter, reduced soils);
- (iii) organic matter complexes (moderate to high organic matter soils);
- (iv) cyanide complexes (influenced by plant roots?).

The large number of potential gold complexes may explain the significant redistribution of gold in many soils and upper weathered horizons (Yassoglou and Nobeli, 1968; Smith and Keele, 1984; Davy and El-Ansary, 1986; Freyssinet *et al.*, 1987; Michel, 1987). Commonly gold is extensively leached from some soil horizons and observed at higher concentrations in other horizons.

8.5 Arid/Acidic Conditions

Arid conditions may overprint previously humid conditions. Thus, over the Yilgarn Block, Western Australia, an old lateritized landscape has experienced arid conditions for several million years, with subsequent modifications of the weathered profile (Butt, 1987). There are also major changes in the groundwater chemistry. The groundwaters have commonly become highly saline. Chloride seems to have been accumulated across the entire area, due to atmospheric accession, with salt aerosol slowly introduced from the ocean and water vapourized (Bettanay *et al.*, 1964; Dimmock *et al.*, 1974; Hingston and Gailitis, 1976). Mann (1983, 1984a,b) suggests that the highly oxidizing and corrosive conditions required for gold chloride solubility (section 4.3) may be achieved in the upper water table and capillary zone of lateritic profiles due to ferrolisis (section 3.5) within these saline groundwaters. Analyses of waters considered representative of the groundwaters when the gold was mobilized gave pH values commonly between 3 and 4 and chloride concentration above 0.1 M. Under these conditions gold will be solubilized if the solution is close to the surface and equilibrated with atmospheric oxygen.

Unfortunately, though gold-chloride mobilization is or has presumably occurred in these profiles it is not presently possible to date the process. In general, intensive lateritization occurs during periods of high rainfall and oscillating water table, during which it seems unlikely that the highly saline conditions required for gold chloride dissolution could have developed (though gold may have been mobilized through complexing with organic acids or other anions). Instead the saline conditions may have developed during the onset of aridity that slowed down or stopped much of the lateritization over the Yilgarn Block.

8.6 Water Table/Capillary Zone

During profile development the water table may rise or fall, either due to changing climatic conditions or to elevation or decline of the landscape (Butt, 1981). Mann (1984b) and Davy and El-Ansary (1986) describe how the water table in profiles at the Yilgarn Block, Western Australia have had declining water tables and gold mobilization seems to have followed this. Reasons for a high mobility of gold at the water table/capillary zone could be:

- (i) high chloride and low pH in the capillary zone of acid/saline soils;
- (ii) high Eh values at the top of the water table due to dissolved oxygen being equilibrated with the atmosphere.

Under these conditions, the top of the water table may be a significant site for gold mobilization. Above this level there is no saturated flow and below solution conditions may be: (a) more dilute; and (b) less oxidizing; resulting in lowered gold solubility. If the level of the water table has shifted on several occasions then observed zones of gold dispersion may indicate a 'fossil' water level, while dispersion may now be occurring at the present-day water level.

9. SUMMARY AND FURTHER WORK

This report describes particular solution conditions under which gold may be solubilized or precipitated. Data is primarily based on the published literature. However, careful analysis of this data has resulted in several issues being clarified and the domains of gold solubility better defined.

Important complexes, and the conditions under which they will be significant for gold mobility, are hypothesized to be:

(i) $\text{Au}(\text{HS})_2^-$	Sulfide Weathering
	(ii) $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$
(iii) $\text{Au}(\text{CN})_2^-$	Laterite and Soil
	(iv) gold-organic matter
	(v) gold colloids
(vi) AuCl_4^- and AuCl_2^-	Capillary Zone
(vii) $\text{Au}(\text{OH})_2^-$	Arid/Acid Conditions
	Arid/Alkaline Conditions

The mechanisms of gold precipitation are delineated. In particular, gold is readily reduced and precipitated, giving rise to a large number of secondary gold morphologies.

The alteration of primary gold is significant within the weathering profile. Possible mechanisms for alteration are described: in particular a theory of galvanic silver loss is suggested for the widespread

occurrence of low silver rims. These rims can lead to preservation of primary gold grains, and therefore allow determination of the original 'gold signature' of the deposit.

It is suggested that further work on gold dissolution and re-precipitation should be done. Some specific questions are:

- (i) are thio complexes of gold of relevance during acid as well as neutral/alkaline weathering;
- (ii) under what circumstances are gold organic matter complexes soluble;
- (iii) are gold-cyanide complexes important for gold mobility in soils;
- (iv) what role, if any, do colloids play in gold mobility;
- (v) is the thermodynamic data for $\text{Au}(\text{OH})_2^-$ accurate;
- (vi) are the conditions postulated for the dissolution of gold chloride (acid/saline/highly oxidizing) and $\text{Au}(\text{OH})_2^-$ (alkaline/highly oxidizing) at all significant in the natural environment.

It is intended that most of these issues will be addressed within this project. Such data will be useful in understanding the geochemistry of gold during weathering and in developing exploration strategies.

This report should assist workers in this field to more clearly delineate the important geochemical processes leading to gold mobilization for an area of investigation, and may therefore help in developing strategies for geochemical exploration for gold.

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APPENDIX

A: Thermodynamic Database

The database is based on information compiled by Aylward and Findlay (1971), Weast (1983), Webster (1985), and that present in the MINTEQ code. Calculations were performed by hand or using the chemical speciation and mineral equilibration programme PHREEQE. Critical constants are given in Table A1. Note that these represent a subset of those used to in the thermodynamic data file for PHREEQE.

The Eh^0 values for the various gold complexes (given in Table A1) were calculated from K_{stab} , as described below.

Eh^0 for the complex MX_z [$Eh^0(MX_z)$] is calculated according to

$$Eh^0(MX_z) = Eh^0(M^{n+}) - \frac{0.05916}{n.m} \times \log K_{stab}$$

where

$Eh^0(M^{n+}) = Eh^0$ for the metal ion

n = the number of electrons for the reaction

m = number of metal ions in the complex

If the concentration of $Eh^0(MX_z)$ required is reduced c times then the redox potential is given by

$$Eh^0(MX_z)_c = Eh^0(MX_z) - \frac{0.05916}{n.m} \times \log c$$

If the concentration of X is reduced k times then the redox potential is given by

$$Eh^0(MX_z)_k = Eh^0(MX_z) + \frac{0.05916}{n.m} \times z \times \log k$$

Table A1: Stability Constants for Gold and Silver Complexes.

Gold Complexes:			Silver Complexes:		
Complex	log K _{stab}	Eh° /V	Complex	log K _{stab}	Eh° /V
Au ⁺	-28.6	1.68	Ag ⁺	-13.5	0.799
Au ³⁺	-76	1.50	Ag(HS) ⁰	16.2	-0.159
AuS ⁻	23.0	0.319	Ag(HS) ₂ ⁻	18.0	-0.266
Au(HS) ⁰	20.0	0.497	AgS ₂ O ₃ ⁻	8.82	0.277
Au(HS) ₂ ⁻	29.7	-0.077	Ag(S ₂ O ₃) ₂ ³⁻	13.46	0.003
Au ₂ (HS) ₂ S ²⁻	62.8	-0.178	AgSO ₃ ⁻	5.60	0.468
AuS ₂ O ₃ ⁻	8.7	1.165	Ag(SO ₃) ₂ ³⁻	8.68	0.286
Au(S ₂ O ₃) ₂ ³⁻	26.0	0.142	Ag(SO ₃) ₃ ⁵⁻	9.00	0.267
AuSO ₃ ⁻	10.4	1.065	AgSO ₄ ⁻	1.3	0.722
Au(SO ₃) ₂ ³⁻	23.0	0.319	AgCl ⁰	3.04	0.619
AuCl ⁰	4.7	1.402	AgCl ₂ ⁻	5.24	0.489
AuCl ₂ ⁻	9	1.148	AgCl ₃ ²⁻	5.6	0.468
AuClOH ⁻	16.5	0.704	AgCl ₄ ³⁻	6.14	0.436
AuOH ⁰	11.9	0.976	Ag ₂ Cl ⁺	4.60	0.663
Au(OH) ₂ ⁻	21.9	0.384	Ag ₃ Cl ²⁺	4.96	0.701
AuCl ₂ ⁺	11.1	1.281	AgOH ⁰	2.0	0.681
AuCl ₂ ⁺	17.6	1.153	Ag(OH) ₂ ⁻	3.99	0.563
AuCl ₃ ⁰	21.6	1.074	Ag ₂ OH ⁺	7.39	0.581
AuCl ₄ ⁻	25.2	1.003	AgNH ₃ ⁺	3.26	0.606
AuCl ₃ OH ⁻	33.1	0.847	Ag(NH ₃) ₂ ⁺	7.22	0.372
AuCl ₂ (OH) ₂ ⁻	39.9	0.713	Ag(CN) ₂ ⁻	19.85	-0.375
AuCl(OH) ₃ ⁻	45.9	0.595	Ag(CN)OH ⁻	13.22	0.017
AuOH ₂ ⁺	16.0	1.184	Ag(SCN) ₂ ⁻	8.39	0.303
Au(OH) ₂ ⁺	32.0	0.869	Ag(SCN) ₄ ³⁻	9.81	0.219
Au(OH) ₃ ⁰	48.9	0.536	AgF ⁰	0.38	0.777
Au(OH) ₄ ⁻	51.1	0.492	AgBr ⁰	4.38	0.540
Au(OH) ₅ ²⁻	51.8	0.479	AgBr ₂ ⁻	7.93	0.330
Au(NH ₃) ₂ ⁺	27	0.083	AgBr ₃ ²⁻	8.53	0.294
Au(NH ₃) ₄ ³⁺	30	0.908	AgBr ₄ ³⁻	8.51	0.296
Au(CN) ₂ ⁻	38.3	-0.586	Ag ₃ Br ²⁺	8.13	0.639
Au(CN) ₄ ⁻	56	0.396	AgI ⁰	6.58	0.410
Au(SCN) ₂ ⁻	25	0.201	AgI ₂ ⁻	15.74	-0.132
Au(SCN) ₄ ⁻	42	0.672	AgI ₃ ²⁻	14.0	-0.029
AuBr ₂ ⁻	12	0.970	Ag ₂ I ⁺	11.0	0.474
AuBr ₄ ⁻	32	0.869	Ag ₃ I ²⁺	13.62	0.531
AuI ₂ ⁻	20.2	0.485	Ag(NO ₂) ⁻	2.30	0.663

Table A2: Solubility Products for Gold and Silver Precipitates.

Gold Compounds:		Silver Compounds:	
Compound	log K_{sol}	Compound	log K_{sol}
AuCl(s)	-8.7	AgCl(s)	-9.75
AuCl ₃ (s)	-15.5	AgBr(s)	-12.31
AuCl ₃ ·2H ₂ O(s)	-14.3	AgI(s)	-16.08
AuBr(s)	-26.2	AgOH(s)	-7.71
AuI(s)	-20.1	Ag ₂ S(s)	-49.2
Au(OH) ₃ (s)	-44.1	Ag ₂ SO ₃ (s)	-13.8
Au ₂ O ₃ (s)	1.4	Ag ₂ SO ₄ (s)	-4.84

Table A3: Dissociation Constants of Acids.

Compound	log K_{a1}	log K_{a2}
H ₂ O	-14.0	-
NH ₄ ⁺	-9.24	-
HCN	-9.22	-
HSCN	-0.85	-
HNO ₂	-3.14	-
HNO ₃	1.37	-
H ₂ S	-7.02	-12.89
H ₂ S ₂ O ₃	> 0	-1.98
H ₂ SO ₃	-1.90	-7.20
H ₂ SO ₄	> 0	-1.99
H ₂ CO ₃	-6.35	-10.33

Table A4: Standard Electrode Potentials.

Reaction	Eh°/V	log K
Au ⁺ + e ⁻ = Au(s)	1.68	28.4
Au ³⁺ + 3e ⁻ = Au(s)	1.50	76
Ag ⁺ + e ⁻ = Ag(s)	0.80	13.51
Fe ³⁺ + e ⁻ = Fe ²⁺	0.77	13.0
MnO ₂ (s) + 4H ⁺ + 2e ⁻ = Mn ²⁺ + 2H ₂ O	1.23	41.6
Mn ³⁺ + e ⁻ = Mn ²⁺	1.49	25.2
NO ₃ ⁻ + 3H ⁺ + 2e ⁻ = HNO ₂ + H ₂ O	0.94	31.6
NO ₃ ⁻ + 10H ⁺ + 8e ⁻ = NH ₄ ⁺ + 3H ₂ O	0.88	119.2
2NO ₃ ⁻ + 12H ⁺ + 10e ⁻ = N ₂ (g) + 6H ₂ O	1.25	210.5
SO ₄ ²⁻ + 4H ⁺ + 2e ⁻ = H ₂ SO ₃ + H ₂ O	0.17	5.8
2H ₂ SO ₃ + 2H ⁺ + 4e ⁻ = S ₂ O ₃ ²⁻ + 3H ₂ O	0.40	27.0
H ₂ SO ₃ + 4H ⁺ + 4e ⁻ = S(s) + 3H ₂ O	0.45	30.4
1/2 S ₄ O ₆ ²⁻ + e ⁻ = S ₂ O ₃ ²⁻	0.08	1.4
S(s) + 2e ⁻ = S ²⁻	-0.48	-16.1

B: Calculations of Silver Activities for Electrum

Data from Table B1 is illustrated graphically in Fig. 9, which is given in the main text (section 6).

Table B1: Silver Activity vs mole % in Electrum*.

Electrum Fineness	[Ag] mole%	Silver Activity Coefficient	Silver Activity a_{Ag}	Gold Activity Coefficient	Gold Activity a_{Au}
18	99	1.00	0.99	0.10	0.001
36	98	0.99	0.97	0.11	0.002
88	95	0.99	0.94	0.13	0.006
170	90	0.97	0.88	0.16	0.02
310	80	0.90	0.72	0.25	0.05
440	70	0.79	0.56	0.37	0.11
650	50	0.55	0.28	0.63	0.31
810	30	0.35	0.10	0.86	0.60
880	20	0.27	0.05	0.94	0.75
940	10	0.21	0.02	0.99	0.89
970	5	0.18	0.009	0.99	0.94
989	2	0.17	0.003	1.00	0.98
994	1	0.16	0.002	1.00	0.99

* Calculated from White *et al.* (1957)

This table is used to determine the resultant silver activity and solubility as follows. The E_h^0 for leaching of silver from electrum [$E_h^0(el)$] is given by the equation:

$$E_h^0(el) = E_h^0(Ag) - 0.05916 \times \log(a_{Ag})$$

where

$E_h^0(Ag)$ = E_h^0 for the oxidative dissolution of pure silver metal

a_{Ag} = the activity of silver for the particular electrum as given in the above table

Electrum 810 fine is used as an example. The silver activity (far right column) is 0.1 times that of silver metal. Thus, $E_h^0(el)$ is given by:

$$\begin{aligned} E_h^0(el) &= E_h^0(Ag) - 0.05916 \times \log(0.1) \\ &= E_h^0(Ag) + 0.059 \end{aligned}$$

Thus, the E_h for dissolution of silver from 810 fine electrum is 0.059 V greater than that for dissolution from pure silver metal.

Electrum 994 fine has a silver activity 0.002 times that of silver metal and the E_h for silver leaching is given by:

$$\begin{aligned} \text{Eh}^{\circ}(\text{el}) &= \text{Eh}^{\circ}(\text{Ag}) - 0.05916 \times \log(0.002) \\ &= \text{Eh}^{\circ}(\text{Ag}) + 0.160 \end{aligned}$$

The Eh of AuCl_2^- is 1.148 and the Eh of AgCl_2^- is 0.489; a difference of 0.659. Thus, for the silver to have the same solubility as gold in electrum the $\text{Eh}^{\circ}(\text{el})$ for the silver will have to be raised by 0.659. This corresponds to

$$\begin{aligned} -0.05916 \times \log(a_{\text{Ag}}) &= 0.659 \\ a_{\text{Ag}} &= 7 \times 10^{-12} \end{aligned}$$

Given an activity coefficient of 0.156 this gives 5×10^{-9} mole% Ag or a fineness of the order of 999.99999998 fine.

If the gold and silver solubilities are being controlled by thiosulfate then the $\text{Eh}^{\circ}(\text{el})$ is required to be raised by 0.139, which corresponds to $a_{\text{Ag}} = 0.0045$. Given an activity coefficient of 0.17 this gives 2.6 mole% Ag or 985 fine.

Similar calculations were performed to give the equilibrium silver contents of electrum equilibrated with various ions, with results as given in Table 5.

C: Gold Solubility Calculations

(i) Pure Water

As shown in Fig. 3, the only complex present in solution at greater than 10^{-6} M was $\text{Au}(\text{OH})_2^-$. K_{stab} of the complex is $10^{21.9}$. The E_h° of this complex is given by:

$$\begin{aligned} E_h^\circ[\text{Au}(\text{OH})_2^-] &= E_h^\circ[\text{Au}^+] - 0.05916 \times \log [K_{\text{stab}}] \\ &= 1.68 - 1.30 \\ &= 0.38 \text{ V} \end{aligned}$$

This E_h° value is for a standard state where all species are at an activity of 1 M. Decreasing the required concentration of $\text{Au}(\text{OH})_2^-$ to 10^{-6} M decreases the required E_h as shown:

$$\begin{aligned} E_h &= E_h^\circ + 0.05916 \times \log [\text{Au}(\text{OH})_2^-] \\ &= 0.38 - 0.35 \\ &= 0.03 \text{ V} \end{aligned}$$

Conversely decreasing the OH^- concentration will increase the E_h for dissolution:

$$\begin{aligned} E_h &= E_h^\circ - 0.05916 \times 2 \cdot \log [\text{OH}^-] \\ &= E_h^\circ + 0.05916 \times 2 \cdot (14 - \text{pH}) \end{aligned}$$

Combining the two equations the E_h for dissolution of 10^{-6} M $\text{Au}(\text{OH})_2^-$ is given by

$$E_h = 1.69 - 0.118 \times \text{pH}$$

Calculated data for dissolution of this complex at 10^{-6} M is given in Table C1. Note that below pH 8 $\text{Au}(\text{OH})_2^-$ is no longer stable, relative to the $\text{O}_2/\text{H}_2\text{O}$ couple.

Table C1: E_h vs pH for $[\text{Au}(\text{OH})_2^-] = 10^{-6}$ M.

pH	$E_h(\text{V})$
8	0.74
9	0.62
10	0.50
11	0.38
12	0.27

(ii) Chloride Solution

The two gold chloride complexes of importance are AuCl_2^- and AuCl_4^- . The E_h for dissolution of 10^{-6} M Au is calculated in a similar manner as above, giving

$$E_h[\text{AuCl}_2^-] = 0.79 - 0.118 \times \log [\text{Cl}^-]$$

and

$$\text{Eh}[\text{AuCl}_4^-] = 0.89 - 0.079 \times \log [\text{Cl}^-]$$

The data is summarized in Table C2.

Table C2: Eh vs [Cl] for gold-chloride solubility = 10^{-6} M.

[Cl]	Eh(V)	
	AuCl_2^-	AuCl_4^-
10^{-5}	1.38	1.28
10^{-4}	1.27	1.20
10^{-3}	1.15	1.12
10^{-2}	1.03	1.04
10^{-1}	0.91	0.96
10^0	0.79	0.88

The chloride activity at which the Eh for dissolution of 10^{-6} M for both complexes is the same is calculated as $10^{-2.3}$ M. Thus, at chloride concentrations at and above this level calculating gold solubilities without using AuCl_2^- will underestimate gold solubility.

D: Silver Solubility Calculations

(i) Pure Water

Reaction is



From this Eh is given by

$$\text{Eh} = 0.7991 + 0.05916 \log[\text{Ag}^+]$$

With results as given in Table D1.

Table D1: Silver Concentration vs Eh for Pure Water.

Eh (V)	[Ag] (M)	[Ag] (mg/L)
0.80	10^0	35000
0.74	10^{-1}	3500
0.68	10^{-2}	350
0.62	10^{-3}	35
0.56	10^{-4}	3.5
0.50	10^{-5}	0.35
0.44	10^{-6}	0.035

(ii) Chloride Solution

To a good approximation silver solubility is limited by the solubility of AgCl in oxidizing solution [i.e. where oxygen fugacity (f_{O_2}) > 10^{-20} (Eh = 0.93 - 0.059 pH)]:

$$K_{\text{sol}} = [\text{Ag}^+].[\text{Cl}^-] = 10^{-9.75}$$

$$\text{and therefore } [\text{Ag}^+] = \frac{10^{-9.75}}{[\text{Cl}^-]}$$

The solubility of the other silver complexes can be calculated by substituting the expression for $[\text{Ag}^+]$ into the equation for the relevant K_{stab} . For example, for AgCl_4^- :

$$\frac{[\text{AgCl}_4^{3-}]}{[\text{Ag}^+].[\text{Cl}^-]^4} = K_{\text{sol}} = 10^{-6.14}$$

substituting in for $[\text{Ag}^+]$ gives

$$\frac{[\text{AgCl}_4^{3-}]}{10^{-9.75} [\text{Cl}^-]^5} = 10^{-6.14}$$

$$\frac{10^{-9.75}}{[\text{Cl}^-]} \times [\text{Cl}^-]^4$$

and thus

$$[\text{AgCl}_4^{3-}] = \frac{10^{-3.61}}{[\text{Cl}^-]^3}$$

Formulas for other silver species are similarly determined. Total silver concentration vs chloride concentration was then determined as summarized in Table D2.

Table D2: Silver Solubility vs Chloride Concentration.

Species	Chloride(M)				
	10 ⁻⁴	10 ⁻³	10 ⁻²	10 ⁻¹	10 ⁰
Ag ⁺	10 ^{-5.8}	10 ^{-6.8}	10 ^{-7.8}	10 ^{-8.8}	10 ^{-9.8}
AgCl ⁰	10 ^{-6.7}	10 ^{-6.7}	10 ^{-6.7}	10 ^{-6.7}	10 ^{-6.7}
AgCl ₂ ⁻	10 ^{-8.5}	10 ^{-7.5}	10 ^{-6.5}	10 ^{-5.5}	10 ^{-4.5}
AgCl ₃ ²⁻	10 ^{-12.2}	10 ^{-10.2}	10 ^{-8.2}	10 ^{-6.2}	10 ^{-4.2}
AgCl ₄ ³⁻	10 ^{-15.6}	10 ^{-12.6}	10 ^{-9.6}	10 ^{-6.6}	10 ^{-3.6}
Ag ₂ Cl ⁺	10 ^{-10.9}	10 ^{-11.9}	10 ^{-12.9}	10 ^{-13.9}	10 ^{-14.9}
Ag ₃ Cl ₂ ⁺	10 ^{-16.7}	10 ^{-18.7}	10 ^{-20.7}	10 ^{-22.7}	10 ^{-24.7}
Total Silver	10 ^{-5.7}	10 ^{-6.4}	10 ^{-6.3}	10 ^{-5.4}	10 ^{-3.5}