

# Gold in Solution

Anthony E. Williams-Jones<sup>1</sup>, Robert J. Bowell<sup>2</sup> and Artashes A. Migdisov<sup>1</sup>

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**Although gold is a noble metal and is effectively insoluble even in strong acids, we have known for nearly 500 years that it can be concentrated to mineable levels by being transported as dissolved species in crustal fluids (indeed, most economic gold deposits owe their origin to this mode of transport). From alchemy and later experimental chemistry and geochemistry, we have developed an understanding of the solubility and speciation of gold in aqueous liquids and other crustal fluids. This knowledge informs us about the processes that promote the transport of gold in the Earth's crust, result in exploitable gold deposits and lead to the remobilization of gold in the surficial environment.**

**KEYWORDS:** gold, solubility, hydrothermal fluids, petroleum, supergene

## INTRODUCTION

Gold is the most noble of all metals. No other metal is less reactive at its surface when in contact with liquids or gases (this helps explain why in nature gold occurs dominantly in its native form), and no other metal is more valued for its resistance to corrosion. Indeed, gold was accorded the status of noble metal because, unlike other metals, it was not known to tarnish or dissolve in strong acids and was therefore deemed incorruptible. However, as early as the 8<sup>th</sup> century CE, Jabir ibn Hayyan (721–815), an Arab alchemist, discovered that gold dissolves in a mixture of three parts hydrochloric acid and one part nitric acid, a liquid that later became known as *aqua regia* (royal water) because of its capacity to dissolve gold (Russell 1686). This capacity, which even today is used in the analysis of gold, results from the fact that nitric acid, an extremely strong oxidant, is able to convert the gold to Au<sup>3+</sup>, thereby making it available for complexation with Cl<sup>-</sup> ions to form aqueous species such as AuCl<sub>4</sub><sup>-</sup>.

During the 17<sup>th</sup> century, the German chemist Georg Stahl (1660–1734), in a quest to explain how Moses was able to turn the golden calf into “bitter water”, found that gold dissolves in aqueous solutions prepared by heating a mixture of *sal mirabilis* (Na<sub>2</sub>SO<sub>4</sub>) and charcoal. He had discovered that gold is soluble in aqueous solutions of NaHS and, as we now know, this occurs because of the complexation of gold to form the species AuHS<sup>o</sup> and Au(HS)<sub>2</sub><sup>-</sup>. However, an equally plausible “bitter water” that Stahl could have considered is colloidal gold, which had been used in

Roman times to make dichroic glass (Fig. 1) and was later promoted by Paracelsus (1493–1541), under the name *aurum potable*, as an elixir of life; the colloidal nature of this deep red fluid was eventually deduced by Michael Faraday (1791–1867).

From an industrial perspective, arguably the most important discovery about the solubility of gold came in the 18<sup>th</sup> century when the Swedish chemist Carl Scheele (1742–1786) found that gold is highly soluble in hydrocyanic acid. This finding eventually led to the patenting of the cyanidation process for refining gold by MacArthur and the Forrest brothers in 1887; the process involves dissolving the gold as Au(CN)<sub>2</sub><sup>-</sup> and reducing it to the native metal with zinc powder. By the early 20<sup>th</sup> century, cyanidation had become the method of choice for the beneficiation of gold ores and remains so to this day.

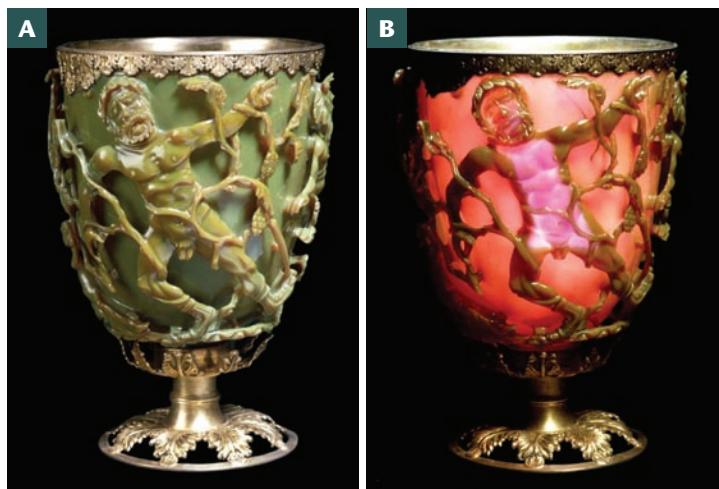
“Now I will discuss that kind of minerals for which it is not necessary to dig, because the forces of water carries them out of the veins”

– Agricola 1556

The idea that gold could be transported in crustal fluids and concentrated as ore can be traced back to the 16<sup>th</sup>-century writings of Agricola (1546) in *De Ortu et Causis Subterraneorum*. This work describes vapours of heated groundwaters mixing with “earth” to form “juices” that rise into fractures, where they deposit metals including gold. Interestingly, however, Jabir ibn Hayyan had noticed some 800 years earlier that waters flowing from copper mines carried scales of copper, which after drying in the desert “contained amongst them the purest gold”. He concluded that the gold was the product of “long washing in water and digestion by the heat of the sun” (Russell 1686), an idea that foreshadows modern thinking about the supergene origin of some of the gold in placer- and regolith-hosted deposits. In the late 17<sup>th</sup> century, the roots of modern hydrothermalism started to take hold, with the proposal by Webster (1671), in his *Metallographia*, that the ore metal is in *principis solutis*, that is, it dissolves in water or steam. This proposal was further developed in the 19<sup>th</sup> century with the observation that dissolution of metals requires “mineralizers” such as B, F, PO<sub>4</sub> and Cl (Daubrée 1841). By the late 19<sup>th</sup> century, hydrothermalism was well established, although opinion continued to be divided well into the 20<sup>th</sup> century over whether the ore-forming fluid is invariably liquid (Graton 1940), or whether, in magmatic-hydrothermal systems, vapour can also play this role (Ingerson and Morey 1940). The issue was finally thought to have been settled when Krauskopf (1957) concluded that the

<sup>1</sup> Department of Earth and Planetary Sciences, McGill University  
3450 University Street, Montreal, Quebec, H3A 2A7, Canada  
Corresponding author: Anthony.Williams-Jones@mcgill.ca

<sup>2</sup> SRK Consulting, Churchill House, Churchill Way  
Cardiff CF10 2HH, Wales, UK



**FIGURE 1** The Lycurgus cup in (A) reflected light and (B) transmitted light. The cup, which depicts the legend of King Lycurgus from Homer's *Iliad*, was made from cut glass for the Roman Emperor Hadrian during the 4<sup>th</sup> century CE. The dichroic quality (green and red colours) is produced by the light-scattering effects of colloidal gold within the glass. COURTESY OF THE BRITISH MUSEUM

volatilities of important ore metals, including gold, are so low at temperatures below 600°C that “simple vapor transport cannot account for the origin of ore deposits”.

Concurrent with the establishment of hydrothermalism in the 19<sup>th</sup> century, it was observed that the fineness (purity) of placer gold increases down drainage and that hexagonal flakes and “fungoid growths” of gold can form at ambient temperature (Liversidge 1893). These observations raised questions about the possible mobilization of gold by surface waters and introduced the idea that supergene processes may play an important role in the dispersal and concentration of gold in the surficial environment.

The first quantitative experiments to investigate the solubility of gold in hydrothermal fluids were by Ogryzlo (1935). Because of the debate over whether metals could be transported in the vapour phase, some of these experiments were conducted with gas mixtures, that is, steam and chlorine gas (used in refining gold ores) and steam and HCl gas. Not unexpectedly, the chlorine–steam mixtures dissolved high (percentage) levels of gold. However, gold was not observed to dissolve in the HCl gas mixtures. The experiments in aqueous liquids were conducted with a variety of solutes, but only solutions containing  $\text{Cl}^-$  or  $\text{HS}^-$  dissolved significant gold. In both cases, gold concentrations exceeded 1000 ppm at 300°C. This work laid the foundations for modern experimental studies by identifying  $\text{HS}^-$  and  $\text{Cl}^-$  as important ligands for the aqueous transport of gold.

## AQUEOUS GEOCHEMISTRY OF GOLD

Pearson (1963) subdivided metals and their ligands (the electron donors with which the metals bond and permit their aqueous dissolution) into two groups: (1) small and strongly charged ions, which he termed “hard”, and (2) large, weakly charged, and highly polarizable ions, which he termed “soft”. Furthermore, he proposed that, where there is competition among ions, hard ions will bond preferentially with hard ligands, and vice versa. In the case of compound ions, however, this classification also considers the valence state of the electron donor or acceptor. Thus, for example, in  $\text{SO}_3^{2-}$ , the electron donor, sulphur, has a valence of +4 and the ion is classified as borderline between hard and soft, whereas in  $\text{HS}^-$ , sulphur has a valence of -2

and the anion is classified as soft. According to the hard–soft classification, gold, which occurs in nature dominantly as  $\text{Au}^+$  or  $\text{Au(I)}$  and is highly polarizable due to a filled  $d$  shell, is considered to be a soft metal and will tend to bond preferentially with soft ligands. Gold also occurs as  $\text{Au(III)}$  but, as discussed below, this harder form is important only under very oxidizing conditions at ambient temperature. An additional characteristic of gold, which relates to its “softness”, is that the outer electron cloud is readily delocalized, allowing for electron transfer and weak bonding between gold atoms. This leads to the formation of clusters with charged surfaces (mainly negative) that repel each other and, in turn, form colloids.

At near-ambient temperature, the most important soft ligands are  $\text{HS}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CN}^-$  and  $\text{SCN}^-$ , the last two being the products of the breakdown of plant matter and algae. Given the importance of  $\text{CN}^-$  in the beneficiation of gold, it is not surprising that  $\text{Au(I)}$  forms its strongest complexes with this ligand [e.g.  $\text{Au(CN)}_2^-$ ]. Next in importance are  $\text{S}_2\text{O}_3^{2-}$  [e.g.  $\text{Au(S}_2\text{O}_3)_2^{3-}$ ], where conditions are oxidizing, and  $\text{HS}^-$  [e.g.  $\text{Au(HS)}_2^-$ ], where conditions are reducing and pH is near to neutral (Vlassopoulos and Wood 1990). Thiocyanate ( $\text{SCN}^-$ ) also forms stable complexes with  $\text{Au(I)}$  but, in environments where it is concentrated, cyanate complexes are likely to predominate. At low concentrations of the above ligands, gold will dissolve predominantly as the hydrolysed species  $\text{AuOH}\cdot(\text{H}_2\text{O})^\circ$  (Vlassopoulos and Wood 1990). Finally, under very oxidizing conditions, such as those of highly saline, acidic groundwaters, gold may be present as  $\text{Au(III)}$  and therefore form stable species with the borderline ligand  $\text{Cl}^-$  (e.g.  $\text{AuCl}_4^-$ ). If, however, the conditions are somewhat less oxidizing and acidic,  $\text{AuCl}_2^-$  will become the dominant gold chloride species, although  $\text{AuOH}\cdot(\text{H}_2\text{O})^\circ$  will predominate (Gammons et al. 1997).

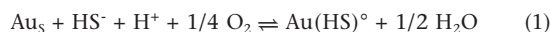
Several studies have documented the dissolution of appreciable quantities of gold in humic and fulvic acids and proposed that organic complexation may also be important in the transport of gold in the surficial environment. However, to date, the only study that has investigated the organic complexation of gold quantitatively is that of Vlassopoulos et al. (1990). These authors employed a variety of organic ligands to act as simple analogues of organic moieties and concluded that the stability of gold organic complexes is greatest with sulphur as the electron donor, very much weaker with nitrogen and even weaker with oxygen.

At elevated temperatures, such as those responsible for the formation of hydrothermal deposits, the speciation of gold is simpler (Figs. 2, 3). The most important ligand at temperatures up to 350°C is  $\text{HS}^-$  (Seward 1973), with  $\text{AuHS}^\circ$  predominating at lower pH and  $\text{Au(HS)}_2^-$  at higher pH (Stefánsson and Seward 2004). The stability constants for these species reach maxima at 350 and 250°C, respectively, due to increased association of  $\text{H}^+$  and  $\text{HS}^-$  as  $\text{H}_2\text{S}$ . This limits their capacity to transport gold at very high temperature. Moreover, the dielectric constant of water decreases with increasing temperature, which favours electrostatic interactions, thereby promoting “hard” behaviour and allowing a soft metallic ion like  $\text{Au}^+$  to form stable bonds with harder anions like  $\text{Cl}^-$  and  $\text{OH}^-$ . Thus, whereas at 25°C the species  $\text{Au(HS)}_2^-$  is about 14 orders of magnitude more stable than the corresponding chloride species ( $\text{AuCl}_2^-$ ), at ~400°C the two species have similar stability constants (Stefánsson and Seward 2004). Consequently, at the higher temperatures of magmatic-hydrothermal systems,  $\text{AuCl}_2^-$  will predominate; the stability of  $\text{AuCl}^\circ$  is too low for this species to be significant. In general,  $\text{AuCl}_2^-$  will tend to dominate under acidic (and oxidizing) conditions,  $\text{Au(HS)}^\circ$  at acidic to intermediate pH and  $\text{Au(HS)}_2^-$  at higher pH (Stefánsson and Seward 2004). In very dilute solutions,  $\text{Au(OH)}^\circ$  may

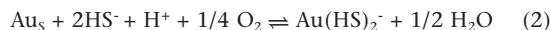
control gold transport at intermediate to alkaline pH, but only at relatively high temperature. This species is, however, less stable than the bisulphide ( $\text{HS}^-$ ) and chloride species and will therefore be subordinate to them, even at relatively low concentrations of  $\text{HS}^-$  and  $\text{Cl}^-$ .

## HYDROTHERMAL TRANSPORT AND DEPOSITION

The dissolution and deposition of gold at temperatures up to about 350°C is controlled by the reactions:



and



Applying Le Châtelier's principle, we can therefore predict that deposition of gold will be promoted by a decrease in the activity of  $\text{HS}^-$  and  $f\text{O}_2$  and an increase in pH.

### Boiling

A decrease in  $\text{HS}^-$  activity could be accomplished by boiling, which would fractionate  $\text{H}_2\text{S}$  strongly into the vapour and lower the activity of  $\text{HS}^-$  via the reaction:



Indeed, this is the favoured mechanism for the precipitation of gold in low-sulphidation (sulphur in a low oxidation state) epithermal systems. Furthermore, boiling increases pH by fractionating acidic components into the vapour, and this also promotes deposition of gold. An additional effect of boiling is the decrease in temperature that accompanies adiabatic expansion of the liquid. However, in some cases (e.g. constant total S), decreasing temperature may actually increase solubility rather than lower it (Fig. 2A). The effect of boiling on  $f\text{O}_2$  contrasts with that on  $\text{HS}^-$  activity and pH. Because hydrogen partitions strongly into the vapour,  $f\text{O}_2$  increases, promoting dissolution of gold.

### Sulphidation

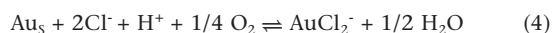
Sulphidation of iron-bearing minerals in the wall rocks to form pyrite is another effective means of reducing  $\text{HS}^-$  concentration. Indeed, this is a frequently proposed explanation for the genesis of mesothermal (orogenic) gold deposits, where hydrothermal alteration commonly involves pyritization and where commonly there is a close spatial association between gold and pyrite.

### Oxidation

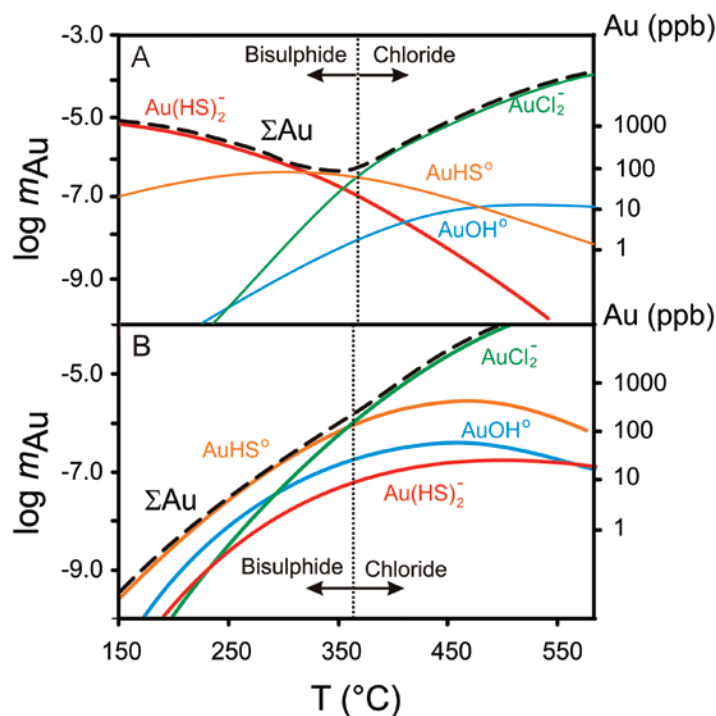
An important feature of the solubility of gold as the species  $\text{Au}(\text{HS})_2^-$  is that its concentration reaches a maximum at  $f\text{O}_2$ -pH conditions close to equi-predominance of the species  $\text{H}_2\text{S}$ ,  $\text{HS}^-$  and  $\text{SO}_4^{2-}$  (Fig. 3). Moreover, a relatively small increase in  $f\text{O}_2$  leads to a precipitous drop in  $\text{HS}^-$  concentration and consequently in gold solubility. As a result, deposition of gold at these conditions is strongly favoured by oxidation and could occur through interaction of the ore-bearing fluid with a hematite-bearing host rock or mixing with oxygenated meteoric waters.

### Cooling

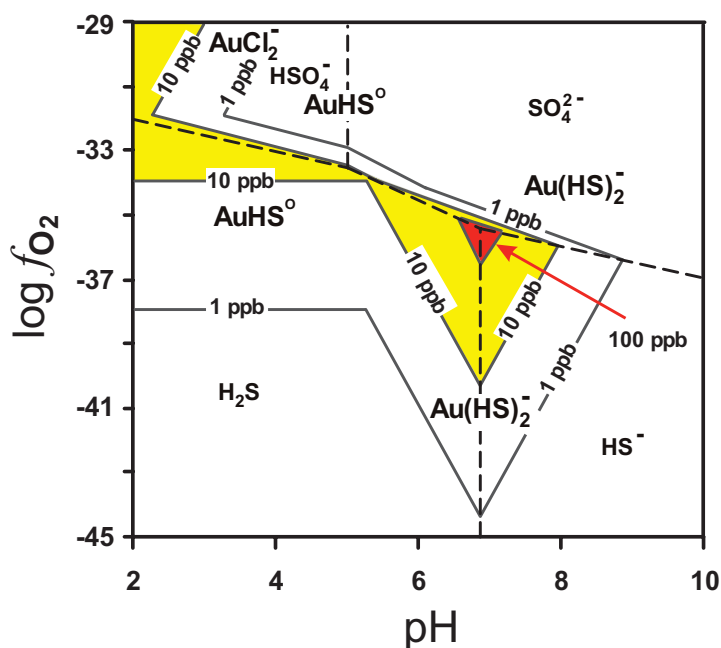
At temperatures above 350°C,  $\text{AuCl}_2^-$  is likely to be the main control on the solubility of gold in chloride-rich systems, such as those forming porphyry copper-gold deposits (Fig. 2). This solubility will be governed by the reaction:



As is the case for reactions 1 and 2, gold deposition is promoted by a decrease in ligand activity and  $f\text{O}_2$ , and by an increase in pH. However, whereas cooling may be rela-



**FIGURE 2** Gold solubility (in terms of molality,  $m$ , and parts per billion) and speciation at 1 kbar as a function of temperature for an aqueous solution containing 1.5 molal ( $m$ ) NaCl and 0.5  $m$  KCl, with pH buffered by the assemblage K-feldspar-muscovite-quartz. (A)  $\Sigma\text{S}$  (total S) = 0.01  $m$  and  $f\text{O}_2$  (oxygen fugacity) is buffered by the assemblage hematite-magnetite. (B)  $\Sigma\text{S}$  and  $f\text{O}_2$  are buffered by the assemblage pyrite-pyrrhotite-magnetite; the maximum value of  $\Sigma\text{S}$  is 0.1  $m$ . The black dashed line ( $\Sigma\text{Au}$ ) indicates the total solubility of gold. The stability constants for gold species are from Stefánsson and Seward (2004), and thermodynamic data for other species are from the SUPCRT92 database (Johnson et al. 1992).



**FIGURE 3** Gold solubility (in parts per billion; solid lines) and speciation at 500 bar and 250°C as a function of  $\log f\text{O}_2$  and pH in a solution containing 1  $m$  NaCl with  $\Sigma\text{S} = 0.01 m$ . The dashed lines separate regions of predominance of  $\text{H}_2\text{S}$ ,  $\text{HS}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$ . Regions of high solubility are highlighted. The stability constants for gold species are from Stefánsson and Seward (2004), and thermodynamic data for other species are from the SUPCRT92 database (Johnson et al. 1992).



tively ineffective in causing large-scale deposition of gold transported as a bisulphide complex, the opposite is true for gold transported as a chloride complex. For example, based on the values of the stability constant of  $\text{AuCl}_2^-$  at 500 bars, a 50°C drop in temperature within the interval 500 to 300°C will result in deposition of over 95% of the gold in solution. Such a drop in temperature is relatively modest for porphyry copper–gold ore-forming systems, where decreases of several hundred degrees are commonplace during the magmatic phase of hydrothermal activity. However, as shown by FIGURE 2, unless the total concentration of sulphur is buffered to much lower values with decreasing temperature (commonly the case; FIG. 2B), after an initial decrease, solubility may actually increase due to the increased stability of bisulphide species, allowing remobilization of the gold into the epithermal environment (FIG. 2A; see also Gammons and Williams-Jones 1997).

## COLLOIDAL PROCESSES

If gold-bearing solutions become supersaturated due, for example, to a sharp drop in temperature, instead of precipitating the gold, they may nucleate negatively charged colloidal particles that repel each other, allowing the gold to remain indefinitely in suspension (a natural *aurum potabile*) and be available for further transport. Commonly, this is accompanied by supersaturation and polymerization of silica, thus forming a suspension of negatively charged colloidal silica particles among which the negatively charged gold particles are dispersed (Saunders 1990). Deposition of gold (e.g. as dendrites in amorphous silica) occurs as a result of flocculation due to changes in the fluid chemistry, such as an increase in salinity or pH, both of which may occur as a result of boiling or fluid mixing. However, colloidal gold may also be adsorbed onto minerals with positive surface charge (p-type conductors), such as arsenian pyrite, a hypothesis that may explain the “invisible” gold in some deposits.

## VAPOUR TRANSPORT

As discussed in the introduction, the idea that vapours may play a role in the hydrothermal transport of metals was thought to have been put to rest by the theoretical study of Krauskopf (1957). However, the discovery of percentage levels of copper in vapour inclusions from the Mole granite (Australia) (Heinrich et al. 1992) and similar concentrations of copper and parts-per-million levels of gold in vapour inclusions from the Bajo de la Alumbrera (Argentina) and Grasberg (Indonesia) porphyry copper–gold deposits (Ulrich et al. 1999) has reopened the debate, particularly as, in all three settings, the concentration of these metals in the vapour exceeded those in the coexisting brine. This has led to proposals that the vapour rather than the liquid may be the main agent of metal transport for copper and gold in porphyry systems.

Since the discoveries mentioned above, several experimental studies have been conducted to investigate the behaviour of metals in water vapour. Their results demonstrate that theoretical estimates based on volatility data grossly underestimate the capacity of this phase to transport metals under hydrothermal conditions, because of a failure to consider the effect of hydration. In the case of gold, Archibald et al. (2001) showed that  $\text{HCl-H}_2\text{O}$  gas mixtures are capable of dissolving up to 10 ppb Au at temperatures similar to those of high-sulphidation (sulphur in a high oxidation state) epithermal systems, due to the formation of  $\text{AuCl} \cdot (\text{H}_2\text{O})_{3-5}$ . This is sufficient to form a deposit containing several tens of metric tons of gold, assuming fluxes and lifetimes of typical hydrothermal systems. More recently, Zevin et al. (2007, 2008) showed

that similar concentrations of gold dissolve in  $\text{H}_2\text{S-H}_2\text{O}$  gas mixtures as  $\text{AuS} \cdot (\text{H}_2\text{S})_2$  and  $\text{AuS} \cdot (\text{H}_2\text{O})_3$ . These concentrations are substantially lower than the parts-per-million concentrations of gold reported in vapour inclusions. However, these inclusions were trapped at temperatures in the range 500 to 600°C and pressures between 500 and 1000 bar, conditions that would have promoted much higher gold solubility than would have been possible at the experimental conditions.

According to the vapour-transport model, which has been applied to both porphyry and epithermal environments, vapour initially condenses some hypersaline liquid at deeper levels where it forms porphyry gold deposits. At subvolcanic levels, the remaining vapour may mix with circulating groundwaters, which subsequently boil to form low-sulphidation gold deposits or condense to an acidic liquid from which high-sulphidation deposits form directly; where the mineralization is late, the high-sulphidation deposits may form from a vapour that contracts to liquid without condensation (Williams-Jones and Heinrich 2005).

## HYDROCARBONS AS A MEDIUM OF TRANSPORT

A crustal fluid that has received little consideration as a possible agent of metal transport is liquid petroleum, despite the fact that it has long been known to commonly contain appreciable concentrations of metals, notably nickel and vanadium, which are used routinely to determine the source of the petroleum. In fact, concentrations of these metals are generally on the order of tens of parts per million and may reach 100 ppm and 1500 ppm, respectively. This metal enrichment and a close spatial and, in some cases, temporal association between gold and hydrocarbons in several deposit types are arguments that liquid petroleum merits consideration as a possible ore fluid.

In the Carlin District (Nevada), hydrocarbons are commonly associated with gold mineralization and, in some deposits, notably along Alligator Ridge, were introduced contemporaneously with the gold, as shown by the presence of oil-bearing fluid inclusions in ore samples (Hulen and Collister 1999). Moreover, Howell et al. (1999) reported amorphous carbon from the Getchell mine containing 915 ppm Au, and Emsbo and Koenig (2007) described veins of pyrobitumen in the El Rodeo deposit containing up to 100 ppm Au. The El Rodeo veins are of particular interest because the gold is homogeneously distributed and the veins have coalesced from underlying microveinlets, suggesting that they record liquid hydrocarbon migration and, in turn, gold mobilization (FIG. 4).

Another mining district where gold is intimately associated with hydrocarbons is the Witwatersrand (South Africa), where 40% of the gold is in reefs with carbon seams, many containing in excess of 1000 ppm Au (Halbauer 1986). On the basis of their organic geochemistry (e.g. Spangenberg and Frimmel 2001) and the occurrence of liquid hydrocarbons preserved as fluid inclusions in overgrowths on detrital quartz grains (England et al. 2002), these seams are now generally considered to represent residues from the migration of liquid hydrocarbons. Proponents of both the modified palaeoplacer and hydrothermal models for the genesis of the Witwatersrand gold deposits have therefore suggested that the hydrocarbons may have promoted deposition of hydrothermally mobilized gold, by reducing  $f\text{O}_2$  and destabilizing  $\text{Au}(\text{HS})_2^-$ . However, the possibility that the hydrocarbons transported gold has been ignored.

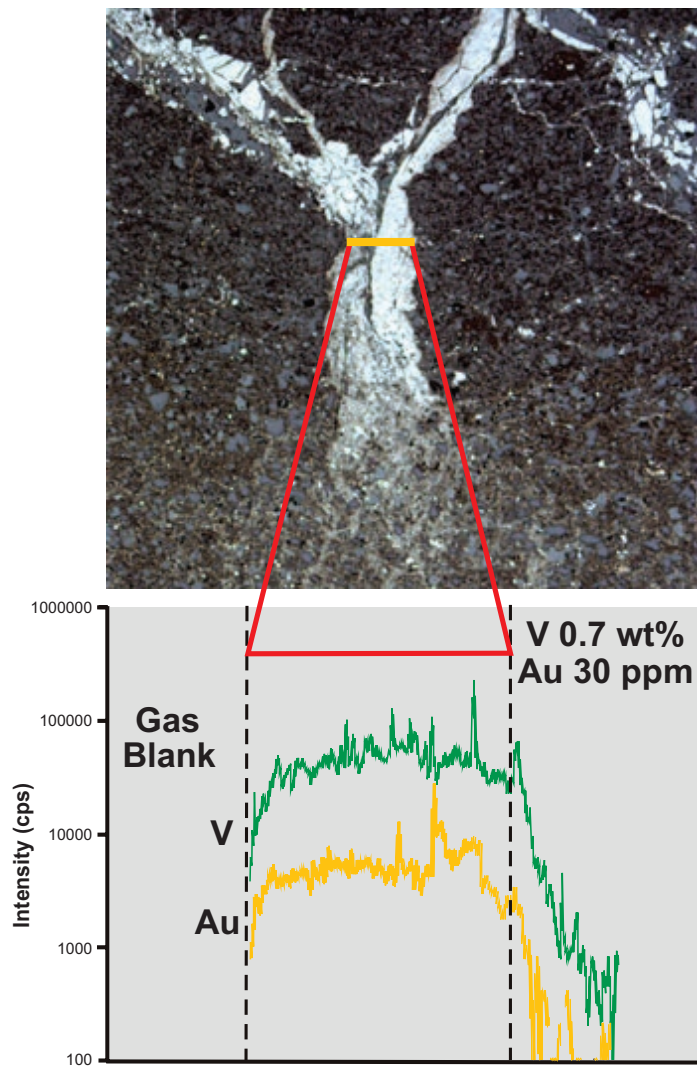
## SUPERGENE CONCENTRATION

The dissolution of gold and its reprecipitation under surface conditions depends on environmental factors and the characteristics of the primary mineralization. Early experimental studies showed the potential for gold remobilization under surface conditions (Machairas 1967) and were supported by mineralogical assessments of placer- and soil-derived gold (Desborough 1970). Regional case studies in Australia, Brazil and Africa provided further evidence of gold mobilization based on particle morphology and chemistry (Fig. 5), as well as on geochemical enrichment patterns and mass balance predictions (summarized in Gray et al. 1992). The determining environmental factors for gold mobilization are geomorphology, climatic conditions, weathering rate, and the physical-chemical characteristics of runoff and groundwater. These are complemented by factors intrinsic to primary gold deposits that are related to the behaviour of the mineralized structures and organic/mineral gangue during weathering. Among them are the permeability of the gangue, its mineralogical composition and the chemical characteristics of the solutions.

The formation of aqueous complexes of gold is strictly dependent on the climatic conditions and the groundwater chemistry generated by mineral–water reactions. Proximal to primary gold deposits, oxidation of sulphides leads to the formation of  $S_2O_3^{2-}$  and the remobilization of gold as the species  $Au(S_2O_3)_2^{3-}$ , provided that pH conditions are neutral to weakly alkaline and the environment is not too oxidizing;  $Au(HS)_2^-$  may be important if conditions are unusually reducing. However, this transport is commonly limited due to subsequent oxidation of the thiosulphate ( $S_2O_3^{2-}$ ) to sulphate (Freyssinet et al. 2005). Beyond the immediate vicinity of the primary deposits, other complexes become more important in controlling gold mobility. For example, in semi-arid to arid environments, such as the gold districts of the southern Yilgarn Craton, Australia, where the groundwater is hypersaline, acidic and oxidizing, gold is transported as halide complexes, predominantly  $AuCl_4^-$ , or possibly as  $AuOH \cdot (H_2O)$  where conditions are slightly less oxidizing and acidic (Gammons et al. 1997; Freyssinet et al. 2005). By contrast, in tropical and equatorial climates, where the soils have high contents of organic matter, gold concentrations in their pore waters correlate well with concentrations of cyanide, ammonia and dissolved organic species (Bowell et al. 1993). Based on their relative stabilities,  $Au(CN)_2^-$  and  $AuOH \cdot (H_2O)$  are interpreted to be the dominant species. However, organic acids may also play an important role in gold transport.

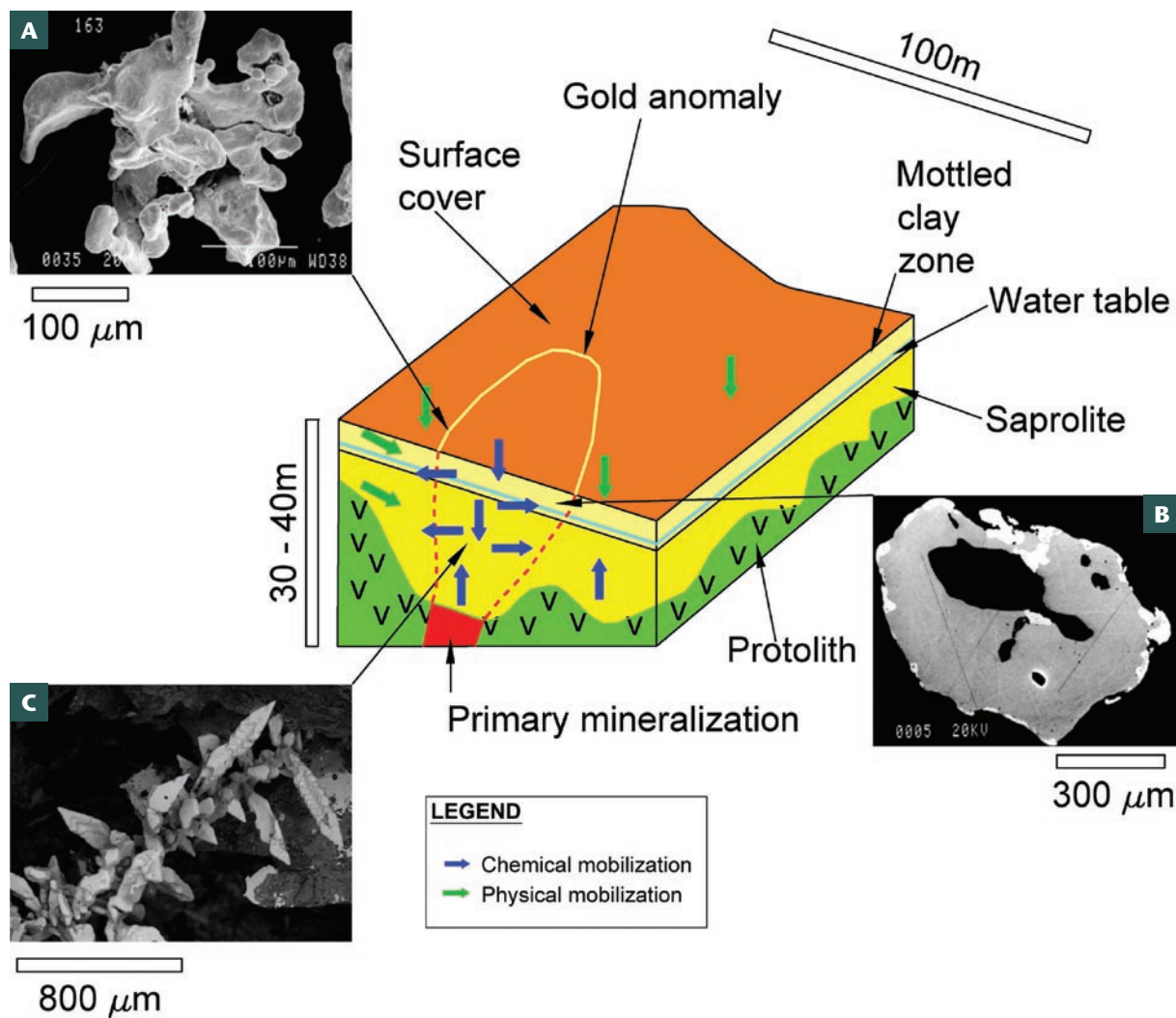
The first studies linking gold genetically to organic matter were based on observations of high gold concentrations in the organic-rich parts of eluvial and palaeoplacer deposits; supported by experiments, Freise (1931) attributed this association to complexing of the gold by organic acids. Other studies, however, have concluded that humic substances merely reduce aqueous gold species, forming colloidal gold, which can then be transported in suspension (Machesky et al. 1992). The critical factor in determining whether organic matter plays a role in gold mobilization is the presence of suitable functional groups on the organic acids to facilitate reduction and/or dissolution. On the basis of experimental data and characterization of soil organic acids, Howell et al. (1993) argued that both reduction and dissolution take place, and that their net effect depends on the magnitudes of the reactions and the rates at which they occur.

Another potentially important means of gold mobilization is via colloidal processes. From the morphology of gold grains collected in Quaternary palaeochannels in the Ampalit and Cempaga-Busang drainage basins in Central Kalimantan,



**FIGURE 4** Pyrobitumen vein containing 30 ppm gold from the El Rodeo deposit, Carlin Trend, Nevada. The uniform nature of the laser ablation ICP-MS gold profile across the vein and its parallelism with the vanadium (V) profile show that both metals are homogeneously distributed and suggest that they are chemically bound in the pyrobitumen. PHOTOGRAPH AND LA-ICP-MS PROFILES SUPPLIED BY P. EMSBO

In order to test the hypothesis that liquid hydrocarbons may play a role in gold transport, Williams-Jones and Migdisov (2007) determined gold's solubility in crude oils at temperatures from 100 to 250°C. Although the upper temperature limit is well above the oil window (the temperature above which liquid petroleum is normally converted to natural gas; 160°C), there is good reason to believe, from pyrolysis experiments and the occurrence of liquid hydrocarbon inclusions preserved in black chimneys, that oil in petroleum reservoirs heated by intrusions or hydrothermal fluids will remain stable for considerable periods of time at temperatures up to 300°C. Thus, if the capacity to dissolve metals is sufficient, liquid petroleum could be a viable ore fluid for gold. The results of the solubility experiments show that crude oil dissolves 2 to 3 ppb Au at 100°C and approximately 50 ppb Au at 250°C. At this stage, we have little understanding of how gold dissolves in hydrocarbons. However, the most plausible explanation is that it bonds to functional groups in asphaltene molecules containing sulphur, nitrogen or oxygen. Similarly, we do not know how the gold may be concentrated, although, given its occurrence in pyrobitumen, distillation is an obvious possibility.



**FIGURE 5** Gold morphology in relation to chemical and physical mechanisms of gold mobilization in a typical tropical regolith, based on *Bowell et al. (1996)*. Physical transport of gold can occur due to profile reduction (erosion) and creep of fine-grained material, whereas chemical mobilization is the product of dissolution and reprecipitation of the gold by groundwater and near-surface soil water. Groundwater in a tropical regolith can flow laterally, downwards and, through evapotranspiration, upwards as well. The gold grains imaged in this figure show morphologies typically observed in the regolith, including (A) “fungoid”-type in the organic-rich soils of the near-surface (reflecting the actions of micro-organisms or dissolution and reprecipitation of the gold by organic acids), (B) rounded grains, commonly with silver-depleted rims, in the clay zone and laterite; and (C) pristine crystals in the matrix of the saprolite.

Indonesia, *Seeley and Senden (1994)* concluded that the gold grains had formed in situ, that is, the gold had been transported as humic acid-stabilized colloids and not as physical grains. More specifically, they proposed that the colloids were carried in groundwater that percolated through the terrace sands and gravels, and when this pregnant groundwater migrated toward the depositional channel, it encountered a “steep chemical gradient” causing the colloids to aggregate near clay zones within the palaeo-channel sands and gravels.

## CONCLUDING REMARKS

During the past 50 years, detailed descriptions of gold deposits, coupled with theoretical and experimental studies, have provided us with a relatively good understanding of how natural waters transport gold and of the mechanisms that may cause its deposition in hypogene and supergene environments. However, recent evidence for gold transport by aqueous vapours in magmatic-hydrothermal systems and proposals that liquid petroleum could transport gold in some environments suggest that not all deposits currently considered to be products of hydrothermal liquids may have formed as envisaged. The challenge for future research dealing with gold in solution will be to expand the current focus on aqueous liquids to include the other fluids known to be present in appreciable volumes in the Earth’s crust. By meeting this broader challenge of embracing all significant crustal fluids in our enquiry, we can expect not only to improve our models of how gold deposits form but also to contribute fundamental scientific knowledge to other fields of geoscience that require an understanding of metal transport.

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## REFERENCES

- Agricola G (1556) *De Re Metallica*. Hoover HC, Hoover LC (translators, 1912). Mining Magazine, London, 637 pp
- Archibald SM, Migdisov AA, Williams-Jones AE (2001) The stability of Au-chloride complexes in water vapor at elevated temperatures and pressures. *Geochimica et Cosmochimica Acta* 65: 4413-4423
- Bowell RJ, Foster RP, Gize AP (1993) The mobility of gold in tropical rain forest soils. *Economic Geology* 88: 999-1016
- Bowell RJ, Laffoley NA, d'Afreh EO, Hanssen E, Abe S, Yao RK, Pohl D (1996) Gold and base metal distribution and exploration in tropical soils: Four contrasting case studies from West Africa. In: Foster RP (ed) *Exploration and Mining in Africa: Towards 2000*. Transactions of the Institute of Mining and Metallurgy 105: B12-33
- Bowell RJ, Baumann M, Gingrich M, Tretbar D, Perkins WF, Fisher PC (1999) The occurrence of gold at the Getchell mine, Nevada. *Journal of Geochemical Exploration* 67: 127-143
- Daubr  e A (1841) M  moire sur le gisement, la constitution et l'origine des amas de min  rai d'  tain. *Annales des Mines*, 3   s  rie, tome XX: 65-112
- Desborough GA (1970) Silver depletion indicated by microanalysis of gold from placer occurrences, western United States. *Economic Geology* 65: 304-311
- Emsbo P, Koenig AE (2007) Transport of Au in petroleum: evidence from the northern Carlin trend, Nevada. In: Andrew CJ et al. (eds) *Proceedings of the 9th Biennial SGA Meeting*, Dublin. Millpress, pp 695-698
- England GL, Rasmussen B, Krapez B, Groves DI (2002) Archean oil migration in the Witwatersrand Basin of South Africa. *Journal of the Geological Society* 159: 189-201
- Freise FW (1931) The transportation of gold by organic underground solutions. *Economic Geology* 26: 421-431
- Freyssinet P, Butt CRM, Morris RC, Piantone P (2005) Ore-forming processes related to lateritic weathering. In: Hedenquist JW, Thompson JFH, Goldfarb RJ, Richards JP (eds) *Economic Geology One Hundredth Anniversary Volume*. Society of Economic Geologists, pp 681-722
- Gammons CH, Williams-Jones AE (1997) Chemical mobility of gold in the porphyry-epithermal environment. *Economic Geology* 92: 45-59
- Gammons CH, Yu Y, Williams-Jones AE (1997) The disproportionation of gold chloride complexes at 25 to 200  C. *Geochimica et Cosmochimica Acta* 61: 1971-1983
- Graton LC (1940) Nature of the ore-forming fluid. *Economic Geology* 35: 197-358
- Gray DJ, Butt CRM, Lawrance LM (1992) The geochemistry of gold in lateritic terrains. In: Butt CRM and Zeegers H (eds), *Regolith Exploration Geochemistry in Tropical and Subtropical Terrains*. Handbook of Exploration Geochemistry, Volume 4. Elsevier, Amsterdam, pp 461-482
- Halbauer DK (1986) The mineralogy and geochemistry of Witwatersrand pyrite, gold, uranium and carbonaceous matter. In: Anhaeusser CR, Maske S (eds) *Mineral Deposits of Southern Africa*. Geological Society of South Africa, Johannesburg, pp 731-752
- Heinrich CA, Ryan CG, Mernagh, TP, Eadington PJ (1992) Segregation of ore metals between magmatic brine and vapor; a fluid inclusion study using PIXE microanalysis. *Economic Geology* 87: 1566-1583
- Hulen JB, Collister JW (1999) The oil-bearing, carlin-type gold deposits of Yankee Basin, Alligator Ridge District, Nevada. *Economic Geology* 94: 1029-1049
- Ingerson E, Morey GW (1940) Nature of the ore-forming fluid: A discussion. *Economic Geology* 35: 772-785
- Johnson JW, Oelkers EH, Helgeson HC (1992) SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000  C. *Computers & Geosciences* 18: 899-947
- Krauskopf KB (1957) The heavy metal content of magmatic vapor at 600 degrees C. *Economic Geology* 52: 786-807
- Liversidge A (1893) On the origin of gold nuggets. *Journal of the Royal Society of New South Wales* 27: 303-343
- Machairas G (1967) Dissolution et recristallisation de l'or primaire pendant l'oxydo-r  duction des sulfures aurif  res. *Bureau de recherches g  ologiques et mini  res bulletin* 5: 111-121
- Machesky ML, Andrade WO, Rose AW (1992) Interactions of gold (III) chloride and elemental gold with peat-derived humic substances. *Chemical Geology* 102: 53-71
- Ogryzlo SP (1935) Hydrothermal experiments with gold. *Economic Geology* 30: 400-424
- Pearson RG (1963) Hard and soft acids and bases. *Journal of the American Chemical Society* 85: 3533-3539
- Russell R (1686) *The Works of Geber* (Translation, edited by EJ Holmyard 1928). Kessinger Publishing, 1997, 306 pp
- Saunders JA (1990) Colloidal transport of gold and silica in epithermal precious-metal systems: Evidence from the Sleeper deposit, Nevada. *Geology* 18: 757-760
- Seeley JB, Senden TJ (1994) Alluvial gold in Kalimantan, Indonesia: A colloidal origin. *Journal of Geochemical Exploration* 50: 457-478
- Seward TM (1973) Thio complexes of gold and the transport of gold in hydrothermal ore solutions. *Geochimica et Cosmochimica Acta* 37: 379-399
- Spangenberg JE, Frimmel HE (2001) Basin-internal derivation of hydrocarbons in the Witwatersrand Basin, South Africa: evidence from bulk and molecular  $\delta^{13}\text{C}$  data. *Chemical Geology* 173: 339-355
- Stef  nsson A, Seward TM (2004) Gold(I) complexing in aqueous sulphide solutions to 500  C at 500 bar. *Geochimica et Cosmochimica Acta* 68: 4121-4143
- Ulrich T, G  nther D, Heinrich CA (1999) Gold concentrations of magmatic brines and the metal budget of porphyry copper deposits: *Nature* 399: 676-679
- Vlassopoulos D, Wood SA (1990) Gold speciation in natural waters: I. Solubility and hydrolysis of gold in aqueous solution. *Geochimica et Cosmochimica Acta* 54: 3-12
- Vlassopoulos D, Wood SA, Mucci A (1990) Gold speciation in natural waters: II. The importance of organic complexing—Experiments with simple model ligands. *Geochimica et Cosmochimica Acta* 54: 1575-1586
- Webster J (1671) *Metallographia: or An History of Metals*. Walter Kettilby, London, 389 pp
- Williams-Jones AE, Heinrich CA (2005) Vapor transport of metals and the formation of magmatic-hydrothermal ore deposits. *Economic Geology* 100: 1287-1312
- Williams-Jones AE, Migdisov AA (2007) The solubility of gold in crude oil: implications for ore genesis. In: Andrew CJ et al. (eds) *Proceedings of the 9th Biennial SGA Meeting*, Dublin. Millpress, pp 765-768
- Zezin DY, Migdisov AA, Williams-Jones AE (2007) The solubility of gold in hydrogen sulfide gas: An experimental study. *Geochimica et Cosmochimica Acta* 71: 3070-3081
- Zezin DY, Migdisov AA, Williams-Jones AE (2008) The solubility of gold in  $\text{H}_2\text{O}-\text{H}_2\text{S}$  vapour. *Geochimica et Cosmochimica Acta* 72 (Supplement 1): A1076

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