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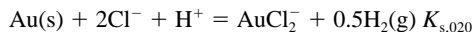
## Stability of chloridogold(I) complexes in aqueous solutions from 300 to 600°C and from 500 to 1800 bar

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**Abstract**—The solubility of gold has been measured in the system  $\text{H}_2\text{O}+\text{H}_2+\text{HCl}+\text{NaCl}+\text{NaOH}$  at temperatures from 300 to 600°C and pressures from 500 to 1800 bar in order to determine the stability and stoichiometry of chloride complexes of gold(I) in hydrothermal solutions. The experiments were carried out in a flow-through autoclave system. This approach permitted the independent determination of the concentrations of all critical aqueous components in solution for the determination of the stability and stoichiometry of gold(I) complexes. The solubilities (i.e. total dissolved gold) were in the range  $9.9 \times 10^{-9}$  to  $3.26 \times 10^{-5}$  mol  $\text{kg}^{-1}$  (0.002–6.42 mg  $\text{kg}^{-1}$ ) in solutions of total dissolved chloride between 0.150 and 1.720 mol  $\text{kg}^{-1}$ , total dissolved sodium between 0.000 and 0.975 mol  $\text{kg}^{-1}$  and total dissolved hydrogen between  $4.34 \times 10^{-6}$  and  $7.87 \times 10^{-4}$  mol  $\text{kg}^{-1}$ . A nonlinear least squares treatment of the data demonstrates that the solubility of gold in chloride solutions is accurately described by the reactions,



where  $\text{AuCl}_2^-$  predominates in acidic chloride solutions and  $\text{AuOH(aq)}$  in neutral to alkaline chloride and chloride-free solutions. The solubility constant,  $\log K_{s,020}$ , increases with increasing temperature and decreases with increasing pressure from a minimum of  $-5.43 (\pm 0.29)$  at 300°C and 500 bar to a maximum of  $-0.15 (\pm 0.16)$  at 600°C and 1000 bar, with the pressure effects becoming more important with increasing temperature. The equilibrium solubility constant for  $\text{AuOH(aq)}$  has been previously determined by Stefánsson and Seward (2003). The solubility of gold at  $\text{pH} > 5$  was found to be independent of chloride concentration up to 1 mol  $\text{kg}^{-1}$  and identical to the solubility of gold with respect to  $\text{AuOH(aq)}$ . The stability of  $\text{AuClOH}^-$  was estimated to be 3 to 6 orders of magnitude less stable than  $\text{AuOH(aq)}$  and  $\text{AuCl}_2^-$  in hydrothermal solutions. Hence, gold(I) chloride complexes play an important role in transporting gold in aqueous acidic chloride solutions above 400°C. Copyright © 2003 Elsevier Ltd

### 1. INTRODUCTION

Gold(I) has a  $5d^{10}$  electronic configuration and prefers two-fold coordination with any type of ligand able to coordinate to a “soft” metal cation. These complexes may be neutral, positive or negative and are linear with bond angles approaching 180° (Cotton et al., 1999). Three and four fold coordinated gold(I) complexes are known to exist, these having trigonal planar and tetrahedral geometry and generally contain phosphine groups which have a very high affinity for gold(I) (Schmidbaur, 1996). In natural ore forming fluids, the most likely potential ligands for complexation with gold(I) are  $\text{HS}^-$ ,  $\text{Cl}^-$  and  $\text{OH}^-$ , such complexes having two fold coordination. As a consequence, most experimental studies on gold in hydrothermal solutions have focused on gold(I) sulfide complexes (Seward, 1973; Belevantsev et al., 1981; Renders and Seward, 1989; Shenberger and Barnes, 1989; Hayashi and Ohmoto, 1991; Benning and Seward, 1996; Zotov et al., 1996; Baranova and Zotov, 1998; Gibert et al., 1998; Loucks and Mavrogenes, 1999), chloride complexes (Nikolaeva et al., 1972; Henley, 1973; Wood et al., 1987; Zotov et al., 1991; Gammons and Williams-

Jones, 1995; Gammons et al., 1997; Frank et al., 2002) and hydroxide complexes (Baranova et al., 1977; Zotov et al., 1985; Vlassopoulos and Wood, 1990; Stefánsson and Seward, 2003). The above studies indicate that sulfide complexes are very stable but suggest also that chloride and hydroxide complexes may play an important role in transporting gold in acidic to neutral pH hydrothermal solutions having low reduced sulfur activity.

At low temperatures and in acidic chloride solutions, gold(I) forms the dichloridogold(I) complex (Nikolaeva et al., 1972) which hydrolyses at neutral and alkaline pH to form  $\text{AuClOH}^-$ ,  $\text{AuOH(aq)}$  and  $\text{Au(OH)}_2^-$ , respectively (Gadet and Pouradier, 1972; Baranova et al., 1977; Vlassopoulos and Wood, 1990). The stability of  $\text{AuCl(aq)}$  is much lower than  $\text{AuCl}_2^-$  and  $\text{AuOH(aq)}$  and it has therefore not been detected in solubility studies. At high temperatures and pressures, the formation of the chloridogold(I) complexes has been studied by Nikolaeva et al. (1972), Henley (1973), Wood et al. (1987), Zotov et al. (1991), Gammons and Williams-Jones (1995), and Gammons et al. (1997), however, considerable discrepancies exist amongst the results making assessment of the role of chloride complexes of gold(I) in hydrothermal ore solutions difficult. Moreover, the stability of gold(I) complexes in neutral and alkaline chloride solutions at high temperatures and the possible role of  $\text{AuClOH}^-$  in hydrothermal solutions has not been investigated.

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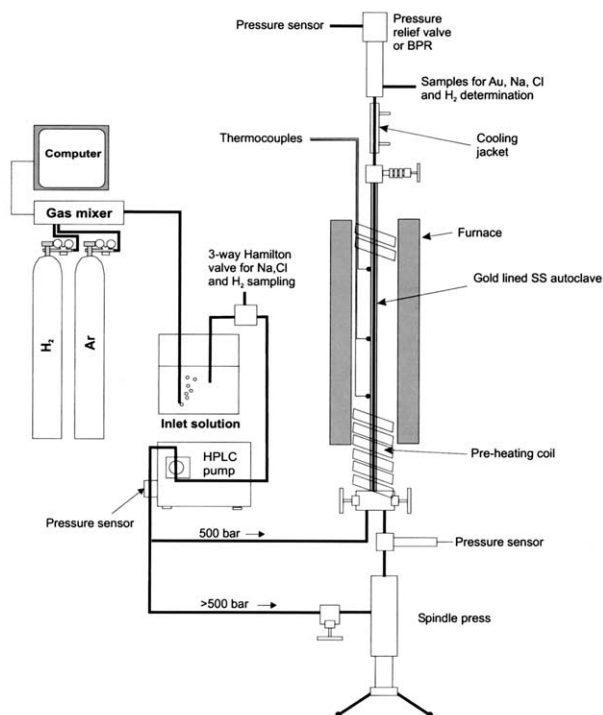


Fig. 1. A schematic diagram showing the experimental setup.

The aim of this study was to determine the stability and stoichiometry of gold(I) complexes at high temperatures and pressures in chloride-containing solutions of acidic to alkaline pH. This was facilitated by measuring the solubility of gold in the system  $\text{H}_2\text{O} + \text{H}_2 + \text{HCl} + \text{NaCl} + \text{NaOH}$ . For this purpose, a flow-through autoclave system was designed and constructed that can be operated up to  $600^\circ\text{C}$  and 2000 bar. This apparatus made it possible to measure independently the concentrations of all components of importance in the system without disturbing the equilibrium conditions.

## 2. EXPERIMENTAL METHODS

The solubility of gold was measured in the system  $\text{H}_2\text{O} + \text{H}_2 + \text{HCl} + \text{NaCl} + \text{NaOH}$ . The solubility measurements were carried out in a flow-through autoclave system (Fig. 1). All the wetted, high pressure parts were constructed of titanium, Hastelloy C276 and gold. The experiments were performed using a stainless steel autoclave lined with gold (99.99%) and filled with gold "sand" having an average grain size of  $\sim 100\ \mu\text{m}$  and total surface area of  $\sim 1\ \text{m}^2$ . The autoclave was 250 mm in length with an internal diameter of 6.5 mm.

The main advantage of using a flow-through autoclave system was that the surface area of gold relative to the total volume of the solution was very high, reducing the time needed to reach equilibrium conditions to minutes and even seconds at high temperatures. Moreover, the experiments were conducted in the single phase field (liquid only or supercritical). This diminishes/eliminates the problems of hydrogen loss, as well as complications in data treatment due to  $\text{H}_2$ ,  $\text{H}_2\text{O}$  and HCl partitioning between two phases. Furthermore, many replicate samples as well as large sample volumes could be taken, thus permitting reliable estimates of the uncertainties of the data.

For the experiments at 500 bar, a High Performance Liquid Chromatographic (HPLC) pump (Varian) supplied the inlet solution to the line and the pressure was controlled by a back-pressure regulator (BPR). For the experiments at 1000 to 1800 bar, the single phase solutions were pressurized and supplied to the line using a spindle-

press and the pressure was regulated by a high pressure relief valve. The pressure was recorded using a pressure transducer in the pressure module of the HPLC pump and an in-line titanium alloy pressure transducer. The readings did not deviate from the set pressure by more than 5 bar at 500 bar and 50 to 100 bar at 1000 to 1800 bar.

The gold-lined stainless steel autoclave was placed in a furnace, the temperature of which was controlled by a temperature controller (Eurotherm<sup>®</sup>) to within  $\pm 2^\circ\text{C}$  of the stated value. Before entering the gold-lined reaction cylinder, the solutions were preheated to the experimental temperature conditions.

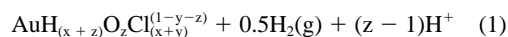
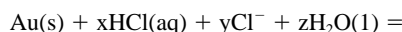
The inlet solutions used in the experiments were prepared from deionised, double-distilled water (in quartz glass), 50% NaOH (Aldrich), 99.99% NaCl (Merck Suprapur<sup>®</sup>) and 30% HCl (Merck Suprapur<sup>®</sup>). All solutions were deoxygenated before use. The redox state was fixed by passing  $\text{H}_2$ -Ar gas mixture through the deoxygenated solution at  $20^\circ\text{C}$  and  $1.2 \pm 0.2$  bar. During the experiments, the same hydrogen partial pressure was maintained over the solution in the inlet solution flask. The gas mixtures were prepared using an EnviroNics computer interfaced gas mixer from either pure or mixtures of hydrogen (SL gas grade 2.0) and deoxygenated argon (SL gas grade 4.8). The hydrogen concentration of the solutions was kept well above the possible production of hydrogen due to breakdown of water at experimental temperatures and pressures.

Liquid samples for determination of dissolved gold, sodium and chloride were collected into polypropylene syringes and samples for dissolved hydrogen were collected using pre-evacuated gas bottles with gas-tight Teflon<sup>®</sup> stopcocks. The samples for gold analyses were prepared, preconcentrated and acidified to 6% HCl (Merck Suprapur<sup>®</sup>) as described by Stefánsson and Seward (2003). The resulting solutions were analysed by flame atomic absorption spectrometry (FAAS) using a Varian 840A spectrometer within 24 h. The precision of the analysis was found to be  $\pm 3\%$  and  $\pm 3 \times 10^{-8}\ \text{mol kg}^{-1}$  above and below  $5 \times 10^{-7}\ \text{mol kg}^{-1}$  at the 95% confidence level. Total chlorine was determined gravimetrically after precipitation with standardised 0.10 mol/L  $\text{AgNO}_3$  solution, with a precision of  $\pm 2\%$  at the 95% confidence level. Total sodium was determined by flame atomic emission spectrometry (FAES), with a precision of  $\pm 3\%$  at the 95% confidence level. The hydrogen and argon concentrations were also measured at isothermal conditions of  $50^\circ\text{C}$  using a gas chromatograph together with a 30 m 5 Å mesh size molecular sieve and a nitrogen carrier gas. These results together with the total mass of solution sampled, the total volume of the sample bottle and the dead volume of the gas chromatograph sample inlet line were used to calculate the dissolved hydrogen concentrations in the experimental solutions and the Ar/ $\text{H}_2$  ratios. The precision of the analyses based on replicated samples was  $\pm 2\%$  at the 95% confidence level.

## 3. AQUEOUS SPECIATION

### 3.1. Speciation Calculations

The dissolution of gold in reduced aqueous chloride solutions assuming only monomeric species to be present can be expressed by the general reaction,



for which the equilibrium solubility constant is

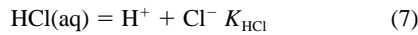
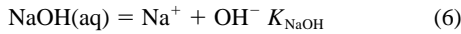
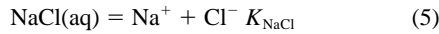
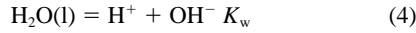
$$K_{xyz} = \frac{a_{\text{AuH}_{(x+z)}\text{O}_z\text{Cl}_{(x+y)}^{(1-y-z)}} a_{\text{H}_2(\text{g})}^{0.5} a_{\text{H}^+}^{(z-1)}}{a_{\text{HCl(aq)}}^x a_{\text{Cl}^-}^y a_{\text{H}_2\text{O(l)}}^z} \quad (2)$$

Gold dissolves to form  $\text{AuOH(aq)}$  in chloride-free, reduced hydrothermal solutions at acid to alkaline pH whereas the free  $\text{Au}^+$  ion is present at negligible concentrations (Stefánsson and Seward, 2003). Accordingly, the total aqueous concentration of gold in aqueous chloride solutions is given by

$$m_{\text{Au,total}} = \sum_x \sum_y \sum_z m_{\text{AuH}_{(x+z)}\text{O}_z\text{Cl}_{(1-y-z)}}^{(1-y-z)} \quad (3)$$

where  $z = 1$  and  $x = y = 0$  for the  $\text{AuOH(aq)}$  species.

In the data treatment, the following species were considered:  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NaCl(aq)}$ ,  $\text{NaOH(aq)}$ ,  $\text{HCl(aq)}$ ,  $\text{H}_2(\text{aq})$  and  $\text{H}_2(\text{g})$  in addition to the speciation model for gold(I) complexes as defined by Eqns. 1 to 3. The relevant independent reactions for the above species are,



For these reactions, the equilibrium constants are given by

$$K_w = m_{\text{H}^+} \gamma_{\text{H}^+} m_{\text{OH}^-} \gamma_{\text{OH}^-} a_{\text{H}_2\text{O}}^{-1} \quad (9)$$

$$K_{\text{NaCl}} = m_{\text{Na}^+} \gamma_{\text{Na}^+} m_{\text{Cl}^-} \gamma_{\text{Cl}^-} m_{\text{NaCl(aq)}}^{-1} \gamma_{\text{NaCl(aq)}}^{-1} \quad (10)$$

$$K_{\text{NaOH}} = m_{\text{Na}^+} \gamma_{\text{Na}^+} m_{\text{OH}^-} \gamma_{\text{OH}^-} m_{\text{NaOH(aq)}}^{-1} \gamma_{\text{NaOH(aq)}}^{-1} \quad (11)$$

$$K_{\text{HCl}} = m_{\text{H}^+} \gamma_{\text{H}^+} m_{\text{Cl}^-} \gamma_{\text{Cl}^-} m_{\text{HCl(aq)}}^{-1} \gamma_{\text{HCl(aq)}}^{-1} \quad (12)$$

$$K_H = m_{\text{H}_2(\text{aq})} \gamma_{\text{H}_2(\text{aq})} f_{\text{H}_2(\text{g})} \quad (13)$$

The solution equilibria are also constrained by the charge balance

$$m_{\text{H}^+} + m_{\text{Na}^+} - m_{\text{Cl}^-} - m_{\text{OH}^-} + \sum_x \sum_y \sum_z (1-y-z) m_{\text{AuH}_{(x+z)}\text{O}_z\text{Cl}_{(1-y-z)}}^{(1-y-z)} = 0 \quad (14)$$

and mass balances

$$m_{\text{Na,total}} = m_{\text{Na}^+} + m_{\text{NaCl(aq)}} + m_{\text{NaOH(aq)}} \quad (15)$$

$$m_{\text{Cl,total}} = m_{\text{Cl}^-} + m_{\text{NaCl(aq)}} + m_{\text{HCl(aq)}} + \sum_x \sum_y \sum_z (x+y) m_{\text{AuH}_{(x+z)}\text{O}_z\text{Cl}_{(1-y-z)}}^{(1-y-z)}, \quad (16)$$

as well as the mass balance equation for aqueous gold species (Eqn. 3) and the proton mass balance.

The ionic strength varied between  $I = 0.0010$  and  $0.66 \text{ mol kg}^{-1}$  and was generally  $< 0.3 \text{ mol kg}^{-1}$  at  $t < 450^\circ\text{C}$  and  $< 0.1 \text{ mol kg}^{-1}$  at  $t > 500^\circ\text{C}$ . Under these conditions, the activity of water can be assumed to be unity and the activity coefficients for neutral aqueous species were also taken as unity. Individual ion activity coefficients were estimated using a modified Debye-Hückel equation (Robinson and Stokes, 1968) of the form

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + \hat{a}B \sqrt{I}} + \Gamma_\gamma + b_\gamma I \quad (17)$$

where  $A$  and  $B$  are the Debye-Hückel parameters,  $z$  is the ionic charge,  $\hat{a}$  is the ion size parameter taken to be 9, 4, 3.5, 3 and  $4 \text{ \AA}$  for  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$  and the gold complexes, respectively (Kielland, 1937),  $\Gamma_\gamma$  is a mole fraction to molality

conversation factor,  $b_\gamma$  is an empirical correction factor characteristic of the bulk electrolyte and  $I$  is the ionic strength.

The aqueous speciation and the determination of the equilibrium constants for the chloridogold(I) complexes in aqueous solutions of low oxidation potential were obtained simultaneously from a nonlinear least squares solution of an expanded form of Eqn. 3 (i.e., by substituting Eqn. 2 into Eqn. 3) at each temperature and pressure with the aid of the FITEQL computer program (Westall, 1982a,b). A subroutine was added to the original program for calculation of ionic strength and individual ion activity coefficients as described above. The equilibrium constants used for the aqueous speciation calculations are given in Table A1, and details of the calculation procedure have been discussed by Stefánsson and Seward (2003).

The dissolved hydrogen concentration of the solutions was calculated from the expression

$$m_{\text{H}_2(\text{aq})} = K_H p_{\text{total}} X_{\text{H}_2(\text{g})} \quad (18)$$

where  $K_H$  is the Henry's law constant for hydrogen in water at  $20^\circ\text{C}$  calculated at the solution ionic strength (Crozier and Yamamoto, 1974),  $p_{\text{total}}$  is the total pressure of the gas phase over the solution and  $X_{\text{H}_2(\text{g})}$  is the mole fraction of hydrogen in the gas phase. The calculated hydrogen concentrations were subsequently corrected for any contribution arising from gold dissolution. For most of the experiments, the total dissolved hydrogen molality was measured using a gas chromatograph. From the dissolved hydrogen concentrations the fugacity of hydrogen was calculated at the experimental temperature and pressure from the Henry's law constant of hydrogen at the respective temperature and pressure (Eqn. 13, Table A1).

A number of gold(I) speciation models were fitted to the data at each temperature and pressure. The goodness of the fit of a given model to the experimental data was quantified with the overall variance,  $V$ , normalised for the number of degrees of freedom

$$V = \frac{\sum \left( \frac{m_{\text{Au}}^{\text{exp}} - m_{\text{Au}}^{\text{calc}}}{s} \right)^2}{n_p n_{\text{II}} - n_u} \quad (19)$$

where  $m_{\text{Au}}^{\text{exp}}$  is the measured gold concentration,  $m_{\text{Au}}^{\text{calc}}$  is the calculated gold concentration,  $s$  is the estimated experimental error,  $n_p$  is the total number of data points,  $n_{\text{II}}$  is the number of components,  $n_u$  is the number of adjustable parameters (i.e., the number of gold(I) species in the model) and the summation is taken over  $p$  data points.

### 3.2. Thermodynamic Database

All the thermodynamic data used for the speciation calculations are given in Table A1 and the equilibrium constants calculated in this study are consistent with these data. The ion product of water (Eqn. 4) was taken from (Marshall and Franck, 1981) who fitted available experimental data to a density function, which is considered reliable to  $1000^\circ\text{C}$  and 10 kbar. The data of Ho and Palmer (1996) and Ho et al. (1994) for the dissociation constants of  $\text{NaOH(aq)}$  (Eqn. 6) and  $\text{NaCl(aq)}$  (Eqn. 5) were selected. These are based on precise conductivity measurements of dilute  $\text{NaOH}$  and  $\text{NaCl}$  solutions, respectively, at elevated temperatures and pressures. We note that the

NaOH(aq) dissociation constants calculated with the SUPCRT92 program are different by 0.5–2.0 log units compared to the values of Ho and Palmer (1996) at the experimental temperatures and pressures of interest in this study.

For the dissociation constant of HCl(aq) (Eqn. 7), the data of Ho et al. (2001) which are also based on conductivity measurements of dilute aqueous HCl solutions at high temperatures and pressures, were selected. The results of Ho et al. (2001) are in a good agreement with those reported by Franck (1956), Wright et al. (1961), Pearson et al. (1963), Lukashov et al. (1975), Ruaya and Seward (1987), and Tagirov et al. (1997) whereas the values reported by Frantz and Marshall (1984) and Lvov et al. (2002) as well as those used in the SUPCRT92 program (Johnson et al., 1992) are only in agreement at  $\rho_w > 0.5 \text{ g cm}^{-3}$ , while below  $0.5 \text{ g cm}^{-3}$  their values are 0.5–2.5 log units lower.

The Henry's law constant for hydrogen in water was used to convert the equilibrium constants from hydrogen molality to hydrogen fugacity. The data used in this study for the Henry's law constant for hydrogen in water are based on experimental data at saturation water vapor pressure (swvp) (Wiebe et al., 1932; Wiebe and Gaddy, 1934; Krichevsky and Kasarnovsky, 1935; Morrison and Billett, 1952; Pray et al., 1952; Stephan et al., 1956; Shoor et al., 1969; Crozier and Yamamoto, 1974; Wiesenburg and Guinasso, 1979; Alvarez et al., 1988) and the high temperature and pressure values of Seward et al. (2000) based on the experimental results of Seward and Franck (1981) at temperatures from 380 to 440°C and pressures up to 2500 bar. The results of Seward and Franck (1981) are in excellent agreement with the independent molecular simulations (histogram-reweighting grand canonical Monte Carlo molecular simulations) on the  $p$ - $V$ - $T$ - $X$  properties of binary  $\text{H}_2$ - $\text{H}_2\text{O}$  fluids of Suleimenov and Seward (2002). On the other hand, the  $p$ - $V$ - $T$ - $X$  results of Kishima and Sakai (1984) are inconsistent with the results of Seward and Franck (1981) and Seward et al. (2000) and the independent molecular simulations of Suleimenov and Seward (2002) and are thus considered spurious. These discrepancies are discussed by Seward et al. (2000). To obtain the Henry's law constants for hydrogen at temperatures below 380°C and pressures between 500 and 1800 bar, the data at saturation water vapor pressure were fitted to generate a smoothed function. These values were subsequently corrected for pressure using the semitheoretical equation of state (EoS) for aqueous nonelectrolytes of Plyasunov et al. (2000). The measured pressure differences for  $K_H$  at 380 to 440°C of Seward et al. (2000) compare closely with those predicted with the EoS of Plyasunov et al. (2000). Moreover, the values at 370°C based on data at saturation water vapor pressure and corrected for pressure according to Plyasunov et al. (2000) are in excellent agreement with the experimental values at 380°C of Seward et al. (2000), thus demonstrating that the experimental and calculated values are consistent with one another. At each isobar, a linear correlation was observed between the Henry's law constant of hydrogen and density of pure water up to at least  $\rho_w = 0.4 \text{ g cm}^{-3}$  and this relationship was used to extrapolate the values to 600°C. The temperature dependence of the Gibbs free energy of reaction and the equilibrium constant can be calculated if the heat capacity of the respective reaction as a function of temperature is known. However, in the case of molecular hydrogen solubility in pure water, the iso-

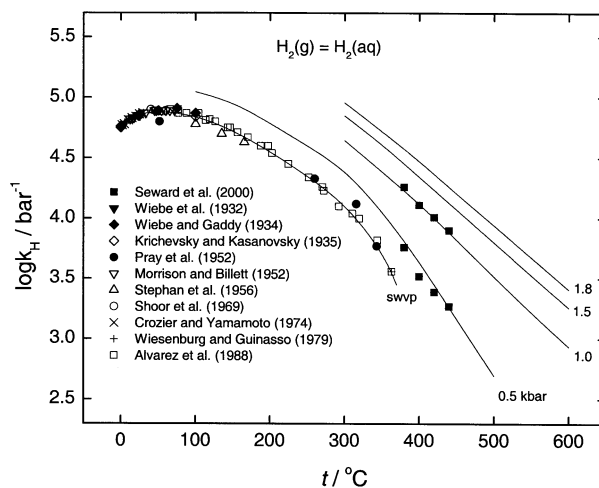


Fig. 2. The temperature and pressure dependence of the Henry's law constant of hydrogen in water. Symbols represent experimentally derived values and the curves smoothed values calculated in this study; swvp denotes saturation water vapor pressure.

baric heat capacity is not known. Moreover, the determination of the heat capacity of reaction from equilibrium constants at low temperature and extrapolation to higher temperatures may incorporate large uncertainties. The simple linear correlation with water density was, therefore, favored. The pressure dependence of the Henry's law constant at  $t > 450^\circ\text{C}$  and 1000 to 1800 bar calculated using density correlation and the EoS of Plyasunov et al. (2000) are almost identical. Finally, all the calculated isobaric values to 600°C were fitted using a quadratic expression to generate smoothed values of the Henry's law constant. These values are compared with the experimental values at different temperatures and pressures in Figure 2 and listed in Table A1. The uncertainties on the values are considered to be less than  $\pm 0.05$  and  $\pm 0.10$  log units at 300–450°C and 450–600°C, respectively.

The gold redox potential has not been experimentally determined at high temperatures and pressures. Therefore, these were calculated using the SUPCRT92 program (Johnson et al., 1992). At 25°C, the SUPCRT92 values are consistent with the values of Bjerrum (1948), Latimer (1952) and Johnson et al. (1978), however, at high temperatures and pressures, the uncertainties on the gold redox potential are unknown.

## 4. RESULTS AND DISCUSSION

### 4.1. Gold Solubility

The solubility of gold has been measured in the system  $\text{H}_2\text{O} + \text{H}_2 + \text{HCl} + \text{NaCl} + \text{NaOH}$  at 300 to 600°C and 500 to 1800 bar (Table A2). The solubilities (i.e., total dissolved gold) were in the range  $9.9 \times 10^{-9}$  to  $3.26 \times 10^{-5} \text{ mol kg}^{-1}$  (0.002–6.42  $\text{mg kg}^{-1}$ ), in solutions of total dissolved chloride between 0.150 and 1.720  $\text{mol kg}^{-1}$ , total dissolved sodium between 0.000 and 0.975  $\text{mol kg}^{-1}$  and total dissolved hydrogen between  $4.34 \times 10^{-6}$  and  $7.87 \times 10^{-4} \text{ mol kg}^{-1}$ .

The aqueous species activities for these solution compositions at the experimental temperatures and pressures were in the range  $a_{\text{Cl}^-} = 10^{-3.2}$ – $10^{-0.77}$ ,  $f_{\text{H}_2(\text{g})} = 10^{-3.5}$ – $10^{-0.80}$  and

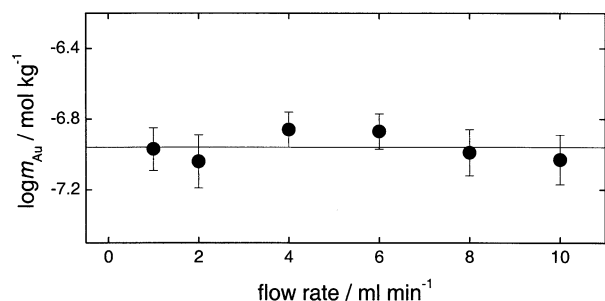


Fig. 3. Gold solubility as a function of flow rate at 300°C and 500 bar and  $m_{\text{Na},\text{total}} = 0.153 \text{ mol kg}^{-1}$ ,  $m_{\text{Cl},\text{total}} = 0.315 \text{ mol kg}^{-1}$  and  $m_{\text{H}_2(\text{aq})} = 3.07 \times 10^{-5} \text{ mol kg}^{-1}$ . A concentration plateau is observed indicating equilibrium solubility.

the calculated  $\text{pH}_{T,p} = 0.6\text{--}11.2$ . With increasing temperature and decreasing pressure the electrolytes became increasingly more associated. For example in solutions of  $m_{\text{Cl},\text{total}} = 0.721 \text{ mol kg}^{-1}$  and  $m_{\text{Na},\text{total}} = 0.135 \text{ mol kg}^{-1}$  at 300°C and 500 bar the calculated pH was 0.74 and the corresponding activities were  $a_{\text{Cl}^-} = 10^{-0.78}$ ,  $a_{\text{HCl}(\text{aq})} = 10^{-0.54}$  and  $a_{\text{NaCl}(\text{aq})} = 10^{-1.58}$  whereas at 500°C and 500 bar the calculated pH was 3.67 and the aqueous species activities were  $a_{\text{Cl}^-} = 10^{-2.60}$ ,  $a_{\text{HCl}(\text{aq})} = 10^{-0.23}$  and  $a_{\text{NaCl}(\text{aq})} = 10^{-0.89}$ . The calculated activities of  $\text{Cl}^-$  and pH are sensitive to the chosen dissociation constants for  $\text{HCl}(\text{aq})$ ,  $\text{NaCl}(\text{aq})$  and  $\text{NaOH}(\text{aq})$  and must be accurately known to reliably assess the equilibrium constants for the formation of gold(I) chloride complexes in aqueous chloride solutions.

Considerable care was taken to establish that the solubilities measured represent equilibrium conditions. This was done in two ways. Firstly, the concentrations of the critical components ( $m_{\text{HCl}}$ ,  $m_{\text{NaOH}}$ ,  $m_{\text{NaCl}}$  and  $m_{\text{H}_2(\text{aq})}$ ) in the inlet solution were varied over a considerable range. Secondly and following Mountain and Seward (1999), a concentration plateau at variable flow rate was considered to indicate equilibrium solubility, as shown for example at 300°C and 500 bar in Figure 3. As indicated, a concentration plateau is observed at all flow rates. The somewhat large scatter in Figure 3 is due to very low solubilities at 300°C.

The gold solubility as a function of measured hydrogen molality is shown in Figure 4 at 350 to 450°C and 500 bar and  $m_{\text{Cl},\text{total}} = 0.413 \text{ mol kg}^{-1}$  and  $m_{\text{Na},\text{total}} = 0.104 \text{ mol kg}^{-1}$ . The slopes of  $-0.48$  to  $-0.54$  indicate that for each mole of gold dissolved, 0.5 mol of  $\text{H}_2$  is produced. These observations demonstrate unambiguously that gold dissolves to form a monovalent gold(I) species in reduced hydrothermal solutions and this was further confirmed in the nonlinear least squares fitting of various speciation models to the data.

The dominant complex stoichiometry and the equilibrium solubility constants were obtained simultaneously with the aqueous speciation calculation using a nonlinear least squares procedure. Gold(I) prefers two-fold coordination with any type of ligand able to coordinate to this soft metal cation (Schmidbaur, 1996; Cotton et al., 1999). The stable aqueous hydroxy complex over the entire pH range of the experiments has been shown to be  $\text{AuOH}(\text{aq})$  (Stefánsson and Seward, 2003). Therefore, the possible stoichiometries in aqueous chloride solutions in addition to the simple hydroxy complex are:  $\text{HAuCl}_2^+$ ,

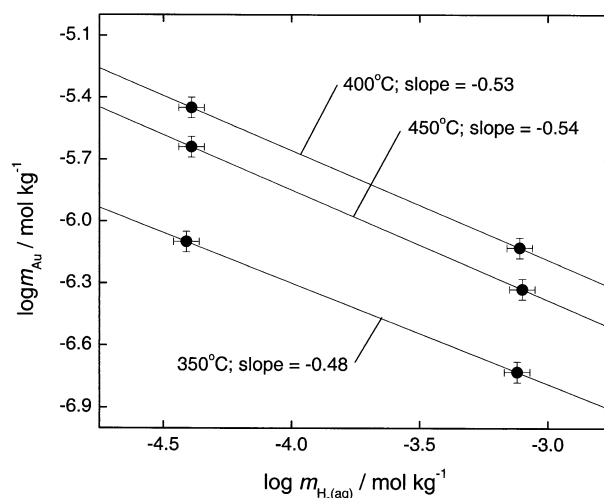


Fig. 4. Gold solubility as a function of measured  $m_{\text{H}_2}$  at 500 bar and  $m_{\text{Cl},\text{total}} = 0.413 \text{ mol kg}^{-1}$  and  $m_{\text{Na},\text{total}} = 0.104 \text{ mol kg}^{-1}$ .

$\text{H}_2\text{AuCl}_2^+$ ,  $\text{HAuCl}_2(\text{aq})$ ,  $\text{AuCl}(\text{aq})$ ,  $\text{AuCl}_2^-$  and  $\text{AuClOH}^-$ . The results of some of the nonlinear least squares fits at 400°C and 500 bar are given in Table 1. As indicated, the model assuming only one gold(I) chloride complex with the  $\text{AuCl}_2^-$  stoichiometry in addition to the  $\text{AuOH}(\text{aq})$  complex resulted in the lowest overall variance and best fitted the experimental data. The same results were obtained at other temperatures and pressures. Thus, gold dissolves in reduced aqueous chloride solutions according to the reactions

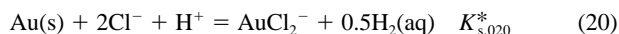


Table 1. Nonlinear least squares fitting for selected gold speciation models to the data at 400°C and 500 bar.

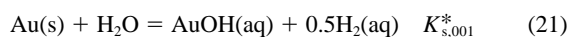
Model no.	Species	$\log K_{s,xyz}$	V
1	$\text{AuOH}(\text{aq})$	$-7.67^a$	52.9
2	$\text{AuOH}(\text{aq})$	$-7.64^b$	1.88
	$\text{AuCl}_2^-$	$-2.80$	
3	$\text{AuOH}(\text{aq})$	$-7.65^a$	17.61
	$\text{AuCl}(\text{aq})$	$-3.93$	
4	$\text{AuOH}(\text{aq})$	$-7.70^a$	55.54
	$\text{Au}(\text{HCl})_2^+$	$-6.32$	
5	$\text{AuOH}(\text{aq})$		No convergence
	$\text{AuHCl}^+$		
6	$\text{AuOH}(\text{aq})$		No convergence
	$\text{HAuCl}_2(\text{aq})$		
7	$\text{AuClOH}^-$		No convergence
	$\text{AuClOH}^-$		
8	$\text{AuClOH}^-$		No convergence
	$\text{AuCl}(\text{aq})$		
	$\text{AuCl}_2^-$		
9	$\text{AuOH}(\text{aq})$		No convergence
	$\text{AuCl}_2^-$		
	$\text{AuOHCl}^-$		
10	$\text{AuOH}(\text{aq})$		No convergence
	$\text{AuCl}(\text{aq})$		
	$\text{AuOHCl}^-$		

<sup>a</sup> The value for  $K_{s,001}$  was fitted as an unknown solubility constant.

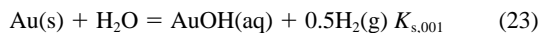
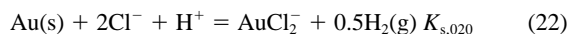
<sup>b</sup> The value for  $K_{s,001}$  was fixed according to the results of Stefánsson and Seward (2003).

Table 2. The experimentally derived equilibrium solubility constant,  $\log K_{s,020}^*$ , for reaction 20 as a function of temperature and pressure; the uncertainties are  $1\sigma$ ; the equilibrium constant is given in terms of hydrogen molality.

$t/^\circ\text{C}$	$\log K_{s,020}^*$			
	500 bar	1000 bar	1500 bar	1800 bar
300	$-6.76 \pm 0.27$	—	—	—
350	$-5.46 \pm 0.06$	—	—	—
400	$-3.75 \pm 0.03$	$-4.78 \pm 0.05$	$-5.21 \pm 0.15$	$-5.44 \pm 0.08$
450	$-1.93 \pm 0.08$	$-3.84 \pm 0.09$	$-4.28 \pm 0.26$	$-4.53 \pm 0.16$
500	—	$-2.85 \pm 0.13$	$-3.55 \pm 0.12$	$-3.92 \pm 0.14$
550	—	$-1.76 \pm 0.06$	$-2.92 \pm 0.03$	$-3.30 \pm 0.11$
600	—	$-0.75 \pm 0.11$	$-2.15 \pm 0.06$	$-2.78 \pm 0.12$



and in terms of hydrogen fugacity



The calculated equilibrium constants as a function of temperature and pressure for  $\text{AuCl}_2^-$  are given in Table 2 with respect to  $m_{\text{H}_2(\text{aq})}$  (Eqn. 20) and in Table 3 with respect to  $f_{\text{H}_2(\text{g})}$  (Eqn. 22) and the latter is plotted in Figure 5. The equilibrium constant,  $\log K_{s,020}$ , increases with increasing temperature from a minimum of  $-5.43 (\pm 0.29)$  at  $300^\circ\text{C}$  and 500 bar to a maximum of  $-0.15 (\pm 0.16)$  at  $600^\circ\text{C}$  and 1000 bar. Moreover, pressure effects also become more important with increasing temperature, the ratio  $K_{s,020}^{1800\text{bar}}/K_{s,020}^{1000\text{bar}}$  is  $10^{-0.48}$  at  $400^\circ\text{C}$  and  $10^{-1.80}$  at  $600^\circ\text{C}$ . The solubility constant with respect to  $\text{AuOH(aq)}$ ,  $K_{s,001}$ , has been previously determined (Stefánsson and Seward, 2003).

The estimated stability and stoichiometry for gold(I) complexes are compared to the measured gold solubility in Figure 6 at fixed solution composition (i.e., the measured gold concentrations were normalised to the same solution composition). The solubility curves were calculated using the results given in Table 3 for  $\text{AuCl}_2^-$  and data from Stefánsson and Seward (2003) for  $\text{AuOH(aq)}$ . As indicated, good agreement is observed between the calculated and measured solubilities.  $\text{AuCl}_2^-$  is observed to be the dominant complex in acidic

Table 3. The experimentally derived equilibrium solubility constant,  $\log K_{s,020}$ , for reaction 22 as a function of temperature and pressure; the uncertainties are  $1\sigma$ ; the equilibrium constant is given in terms of hydrogen fugacity.

$t/^\circ\text{C}$	$\log K_{s,020}$			
	500 bar	1000 bar	1500 bar	1800 bar
300	$-5.43 \pm 0.29$	—	—	—
350	$-4.30 \pm 0.08$	—	—	—
400	$-2.80 \pm 0.05$	$-3.59 \pm 0.07$	$-3.90 \pm 0.17$	$-4.07 \pm 0.10$
450	$-1.22 \pm 0.10$	$-2.80 \pm 0.11$	$-3.11 \pm 0.28$	$-3.29 \pm 0.18$
500	—	$-1.96 \pm 0.18$	$-2.53 \pm 0.17$	$-2.82 \pm 0.19$
550	—	$-1.02 \pm 0.11$	$-2.04 \pm 0.08$	$-2.34 \pm 0.16$
600	—	$-0.15 \pm 0.16$	$-1.39 \pm 0.11$	$-1.95 \pm 0.17$

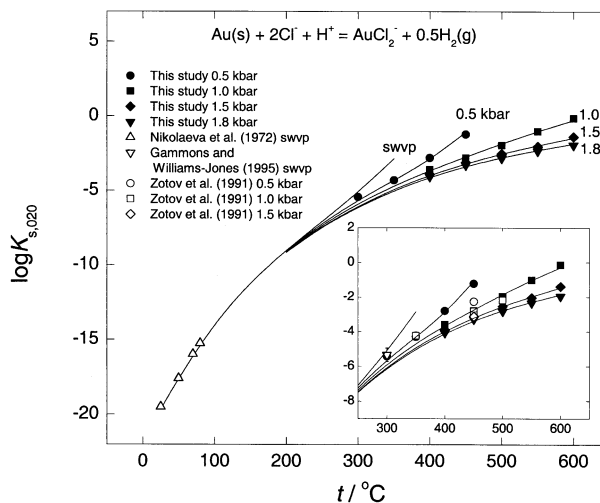
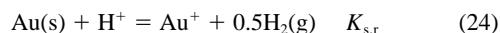


Fig. 5. The logarithm of the solubility constant  $\log K_{s,020}$  as a function of temperature at variable pressures derived in this study (Table 3). The lines represent smoothed solubility constant (Table 5); swvp denotes saturation water vapor pressure.

chloride solutions and  $\text{AuOH(aq)}$  in neutral and alkaline chloride and chloride free solutions.

Smoothed equilibrium constants for the formation of  $\text{AuCl}_2^-$  (i.e.,  $\log K_{s,020}$ , Eqn. 22), were generated by fitting the experimental results separately at each isobar using an extended van't Hoff equation (Table 4). These functions are only considered valid between 300 and  $600^\circ\text{C}$  and 500 and 1800 bar. The results were extrapolated to lower temperatures by adding the dissociation reaction of  $\text{HCl(aq)}$  (Eqn. 7) and subtracting the gold redox potential



from the dissolution reaction of gold to from  $\text{AuCl}_2^-$  (i.e. Eqn. 22) to give



The equilibrium constant for reaction 25 was found to be slightly temperature dependent but pressure independent within errors and fitted to an extended van't Hoff equation to give

$$\log K_2 = 13.57097 - 0.015492T + \frac{280.61527}{T} \quad (26)$$

The pressure independence of  $K_2$  is related to the small  $\Delta V^\circ$  of reaction 25 at the experimental temperatures and pressures. It does not, however, imply that such a relationship holds for all chloride metal reactions and that Eqn. 26 can be extrapolated much outside conditions where experimentally obtained values exists. The smoothed equilibrium constants (i.e.,  $\log K_{s,020}$ , Eqn. 22) were calculated at 300 to  $600^\circ\text{C}$  and 500 to 1800 bar from coefficients given in Table 4 and at  $t < 300^\circ\text{C}$  and  $p > 1800$  bar from the temperature dependence of  $K_2$  (Eqn. 26) and the temperature and pressure dependence of  $K_{s,r}$  (Eqn. 24) and the dissociation constant of  $\text{HCl(aq)}$  (Eqn. 7) (i.e.,  $\log K_{s,020} = \log K_2 + \log K_{s,r} - \log K_{\text{HCl}}$ ). The results are listed in Table 5 and compared with the experimental values in Figure 5.

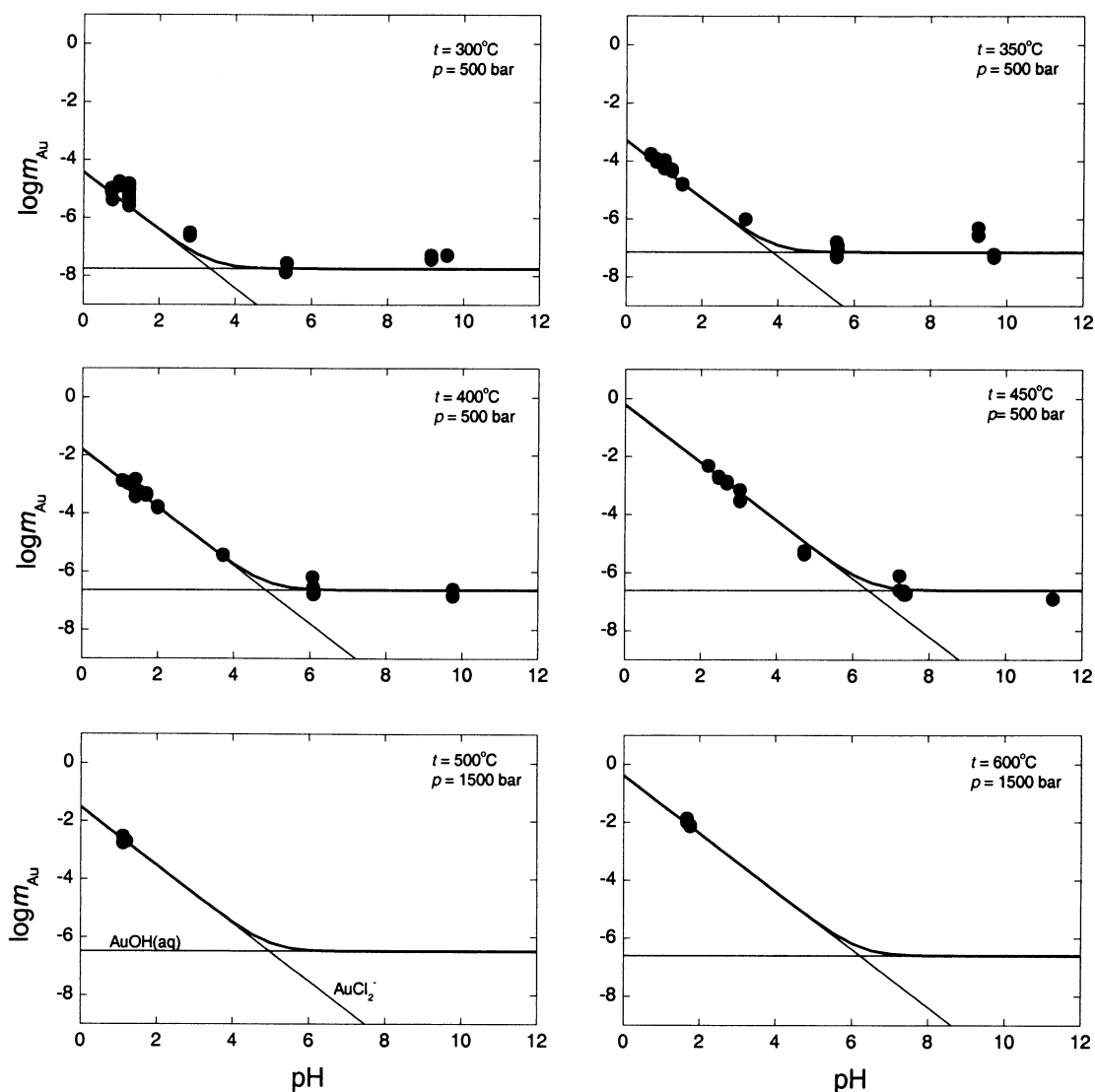
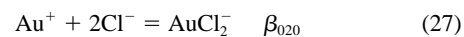


Fig. 6. Gold solubility as a function pH at constant  $a_{\text{Cl}^-} = 1.000 \text{ mol kg}^{-1}$  and  $f_{\text{H}_2} = 0.01 \text{ bar}$ . The experimental points were normalised to the solution composition. The curves represent calculated solubilities contributing from  $\text{AuCl}_2^-$  and  $\text{AuOH(aq)}$  aqueous complexes. The solubility constants  $K_{s,020}$  and  $K_{s,001}$  were taken from Table 3 and (Stefánsson and Seward, 2003), respectively; swvp denotes saturation water vapor pressure.

#### 4.2. Formation Constant and Thermodynamics of Complex Formation

The equilibrium formation constant of  $\text{AuCl}_2^-$ ,  $\beta_{020}$ , according to the reaction



was calculated from the solubility constant of gold  $K_{s,020}$  (Eqn. 22) (Table 3) and the gold redox potential,  $K_{s,r}$  (Eqn. 24) (i.e.,  $\log\beta_{020} = \log K_{s,020} - \log K_{s,r}$ ). The results are given in Table

Table 4. Coefficients describing the temperature variation of  $\log K_{s,020}$  (Eqn. 22) between 300 and 600°C.

$p/\text{bar}$	$\log K_{s,020} = A + BT + C/T + DT^2 + E\log T$				
	$A$	$B$	$C$	$D$	$E$
500	-47.3672	0.048414	8048.92	0.000	0.000
1000	-3.8201	0.009902	-4377.57	0.000	0.000
1500	9.3061	-0.001418	-8289.84	0.000	0.000
1800	14.0125	-0.005494	-9692.53	0.000	0.000

Table 5. The smoothed equilibrium solubility constant,  $\log K_{s,020}$ , for reaction 22 as a function of temperature and pressure; swvp denotes saturation water vapor pressure.

$t/^\circ\text{C}$	$\log K_{s,020}$				
	swvp	500 bar	1000 bar	1500 bar	2000 bar
25	-19.4	-19.4	-19.4	-19.5	-19.5
50	-17.2	-17.2	-17.2	-17.2	-17.3
100	-13.6	-13.6	-13.7	-13.7	-13.7
150	-10.9	-11.0	-11.0	-11.0	-11.0
200	-8.9	-8.9	-8.9	-9.0	-9.0
250	-7.0	-7.1	-7.2	-7.3	-7.3
300	-5.1	-5.58	-5.81	-5.99	-6.1
350	-2.8	-4.27	-4.64	-4.86	-5.0
400	—	-2.84	-3.63	-3.94	-4.2
450	—	-1.22	-2.73	-3.19	-3.5
500	—	—	-1.84	-2.52	-2.9
550	—	—	-1.03	-1.98	-2.5
600	—	—	-0.15	-1.39	-2.1

6 and plotted in Figure 7. The formation constant  $\log \beta_{020}$  has a maximum of  $+6.31 (\pm 0.29)$  at  $300^\circ\text{C}$  and 500 bar and a minimum of  $+3.47 (\pm 0.17)$  at  $600^\circ\text{C}$  and 1800 bar.

The smoothed equilibrium formation constant as a function of temperature and pressure to  $600^\circ\text{C}$  and 2000 bar was calculated from the smoothed solubility constants (Table 5) and the gold redox potential (i.e.,  $\log \beta_{020} = \log K_{s,020} - \log K_{r,0}$ ). The results are listed in Table 7 and plotted in Figure 7. At pressures to 1000 bar, the formation constant decreases with increasing temperature to a minimum and then increases again, whereas at higher pressures, the formation constant decreases with increasing temperature to  $600^\circ\text{C}$ . The formation constant decreases with increasing pressures at all temperatures.

Equation 26 was differentiated with respect to temperature to give the enthalpy of reaction (i.e.,  $RT^2(\partial \ln K_2 / \partial T)_p = \Delta H_{r,K_2}^\circ$ ). As  $K_2$  was observed to be independent of pressure within experimental uncertainties, it follows that the volume of reaction is close to zero (i.e.,  $-RT(\partial \ln K_2 / \partial p)_T = \Delta V_{r,K_2}^\circ$ ). Combining the enthalpy and volume of  $K_2$  with the enthalpy and volume of dissociation of HCl(aq) gives the enthalpy and volume of formation of  $\text{AuCl}_2^-$ ,

$$\Delta H_{r,\beta_{020}}^\circ = \Delta H_{r,K_2}^\circ - \Delta H_{r,K_{\text{HCl}}}^\circ \quad (28)$$

$$\Delta V_{r,\beta_{020}}^\circ = \Delta V_{r,K_2}^\circ - \Delta V_{r,K_{\text{HCl}}}^\circ \quad (29)$$

where the subscripts  $\beta_{020}$ ,  $K_2$  and  $K_{\text{HCl}}$  refer to reactions 27,

Table 6. The cumulative formation constant,  $\log \beta_{020}$ , for reaction 27 as a function of temperature and pressure calculated from the equilibrium solubility constant derived in this study (Table 3) and literature data for  $K_{s,r}$  and  $K_{\text{HCl}}$  (see text); the uncertainties are  $1\sigma$ .

$t/^\circ\text{C}$	$\log \beta_{020}$			
	500 bar	1000 bar	1500 bar	1800 bar
300	$6.31 \pm 0.29$	—	—	—
350	$5.97 \pm 0.08$	—	—	—
400	$6.22 \pm 0.05$	$5.42 \pm 0.07$	$5.11 \pm 0.17$	$4.95 \pm 0.10$
450	$6.72 \pm 0.10$	$5.14 \pm 0.11$	$4.82 \pm 0.28$	$4.64 \pm 0.18$
500	—	$5.03 \pm 0.18$	$4.45 \pm 0.17$	$4.17 \pm 0.19$
550	—	$5.15 \pm 0.11$	$4.11 \pm 0.08$	$3.82 \pm 0.16$
600	—	$5.29 \pm 0.16$	$4.02 \pm 0.11$	$3.47 \pm 0.17$

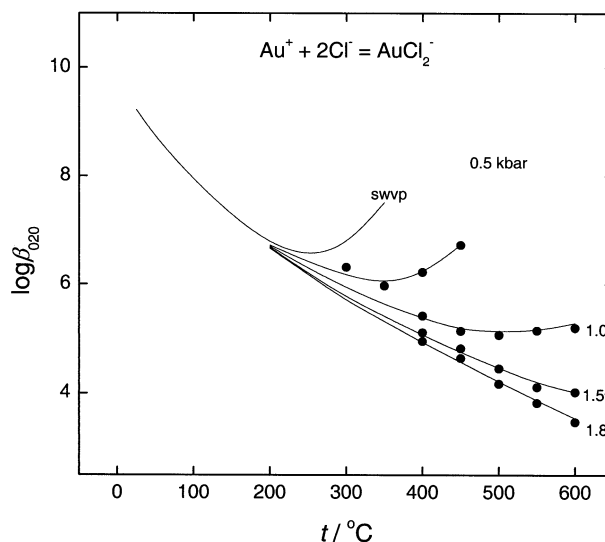


Fig. 7. The logarithm of the formation constant  $\log \beta_{020}$  as a function of temperature at variable pressures derived in this study (Table 6). The lines represent the smoothed formation constant (Table 7); swvp denotes saturation water vapor pressure.

25, and 7, respectively. The enthalpy and volume of dissociation of HCl(aq) were obtained by taking the appropriated derivatives of the density function (Gates et al., 1982; Mesmer et al., 1988) that describes the dissociation constant of HCl(aq) with temperature and water density (pressure) (Ho et al., 2001), combined with the density of pure water and its derivatives (Haar et al., 1984). The entropy of formation of  $\text{AuCl}_2^-$  was subsequently obtained by combining the Gibbs free energy and the enthalpy of reaction 27 (i.e.,  $\Delta G_r = \Delta H_r - T\Delta S_r$ ). The results are plotted in Figure 8. At  $25^\circ\text{C}$ , the cumulative replacement of two  $\text{Cl}^-$  ion by water molecules around the  $\text{Au}^+$  ion is associated with a small exothermic enthalpy and a positive entropy. With increasing temperature and decreasing pressure, the formation of  $\text{AuCl}_2^-$  becomes highly endothermic with a large positive entropy. The reverse is true with increasing pressure and at 2000 bar and  $600^\circ\text{C}$  where the reaction is

Table 7. The smoothed equilibrium formation constant,  $\log \beta_{020}$ , for reaction 27 as a function of temperature and pressure; swvp denotes saturated water vapor pressure.

$t/^\circ\text{C}$	$\log \beta_{020}$				
	swvp	500 bar	1000 bar	1500 bar	2000 bar
25	9.2	9.2	9.2	9.2	9.2
50	8.7	8.7	8.7	8.7	8.7
100	7.9	7.9	7.9	7.9	7.9
150	7.3	7.3	7.3	7.3	7.3
200	6.7	6.7	6.7	6.7	6.6
250	6.5	6.4	6.3	6.2	6.2
300	6.7	6.16	5.94	5.77	5.6
350	7.5	6.01	5.63	5.41	5.3
400	—	6.18	5.38	5.07	4.9
450	—	6.73	5.21	4.75	4.5
500	—	—	5.15	4.46	4.1
550	—	—	5.15	4.19	3.7
600	—	—	5.29	4.02	3.3



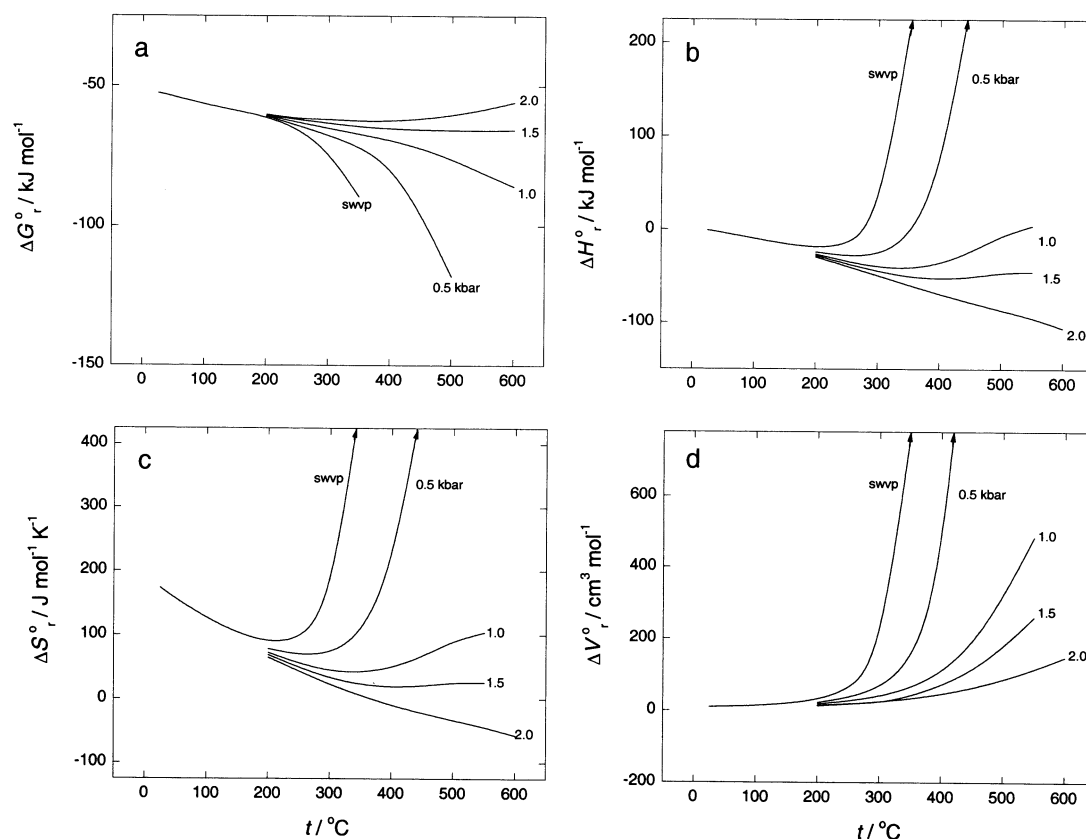


Fig. 8. The (a) Gibbs free energies, (b) enthalpies, (c) entropies and (d) volumes for the cumulative formation of  $\text{AuCl}_2^-$  (Eqn. 27) as a function of temperature and pressure; swvp denotes saturation water vapor pressure.

characterised by an exothermic enthalpy with an accompanying small negative entropy.

### 4.3. Mixed Chloridohydroxygold(I) Complexes

Gadet and Pouradier (1972) studied the complexation of gold(I) with hydroxide and chloride ligands in alkaline solutions at 25°C and 1 bar and concluded that two complexes were present in their solutions,  $\text{Au}(\text{OH})_2^-$  and  $\text{AuClOH}^-$ . They further estimated the equilibrium constant for the reaction



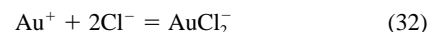
as  $\log K = +6.7 \pm 0.1$ . However, the presence and stability of a mixed  $\text{AuClOH}^-$  complex at high temperatures and pressures is at present unclear. The possible role of such a complex at high temperatures was investigated in this study. It should be noted, however, that the solubility of gold in near neutral to alkaline chloride solutions is described by the presence of  $\text{AuOH}(\text{aq})$  (Stefánsson and Seward, 2003) as shown in Figure 9. Under the conditions of our experiments and associated uncertainties, the presence of  $\text{AuClOH}^-$  could not be unambiguously determined.

The formation constant,  $K_{\text{AuClOH}^-}$ , for the reaction



may be estimated using a statistical approach (Dryssen et al.,

1968; Byrne, 1980) and the equilibrium formation constants for the reactions



where the concentration of  $\text{AuClOH}^-$  in equilibrium with  $\text{AuCl}_2^-$  and  $\text{Au}(\text{OH})_2^-$  is given by

$$m_{\text{AuClOH}^-} = 2(m_{\text{AuCl}_2^-} m_{\text{Au}(\text{OH})_2^-} \gamma_{\text{AuCl}_2^-} \gamma_{\text{Au}(\text{OH})_2^-})^{0.5} \gamma_{\text{AuClOH}^-}^{-1} \quad (34)$$

In the system  $\text{H}_2\text{O} + \text{H}_2 + \text{HCl} + \text{NaCl} + \text{NaOH}$ , aqueous gold(I) can be assumed to be present as  $\text{Au}^+$ ,  $\text{AuOH}(\text{aq})$ ,  $\text{Au}(\text{OH})_2^-$ ,  $\text{AuCl}_2^-$  and  $\text{AuClOH}^-$ . By solving the relevant mass balance and mass action equations, the activities of  $\text{AuCl}_2^-$  and  $\text{Au}(\text{OH})_2^-$  can be determined at a given  $m_{\text{Cl}^-}$  and pH and hence, the molality and activity of  $\text{AuClOH}^-$  and its formation constant may be obtained.

The formation constant of  $\text{Au}(\text{OH})_2^-$  at high temperatures and pressures is unknown at present and previous experimental results indicate that the presence of such complex is not important at least at  $\text{pH}_{T,p} \leq 11$  up to 600°C (Stefánsson and Seward, 2003). If one assigns all the measured dissolved gold concentration in the most alkaline solution to  $\text{Au}(\text{OH})_2^-$ , the maximum equilibrium solubility constant and formation con-

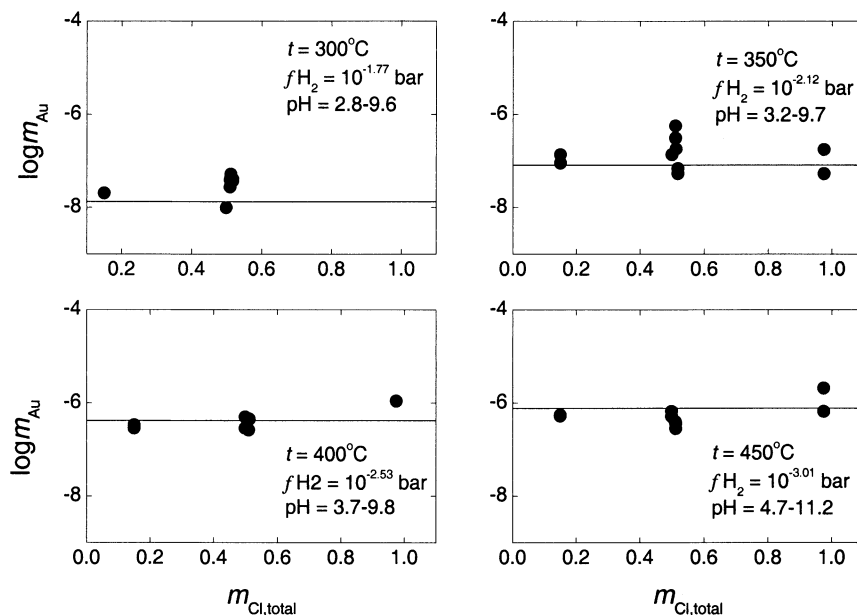


Fig. 9. Gold solubility as a function of  $m_{\text{Cl},\text{total}}$  at fixed  $f_{\text{H}_2(\text{g})}$  in experimental runs having slightly acidic to alkaline pH. The lines represent calculated solubilities to form  $\text{AuOH}(\text{aq})$  using the solubility constant determined by (Stefánsson and Seward, 2003).

stant to form  $\text{Au}(\text{OH})_2^-$  may be estimated from the results of (Stefánsson and Seward, 2003). The resulting constants are listed in Table 8 at various temperatures and pressures. Using the formation constant ( $\beta_{002}$ , Table 8), the formation constant for  $\text{AuCl}_2^-$  ( $\beta_{020}$ , Table 6), the formation constant for  $\text{AuOH}(\text{aq})$  ( $\beta_{001}$ , Stefánsson and Seward, 2003) and  $K_{s,r}$  for the stability of  $\text{Au}^+$  (SUPCRT92, Johnson et al., 1992), the activities of  $\text{AuCl}_2^-$  and  $\text{Au}(\text{OH})_2^-$  at a given solution composition were calculated and subsequently the formation constant for  $\text{AuClOH}^-$  according to reaction 31 was estimated from Eqn. 34. Our estimated values at  $25^\circ\text{C}$  and 1 bar of  $\log K_{\text{AuClOH}} = +15.9$  compare well with the experimentally determined value

of  $\log K_{\text{AuClOH}} = +15.7 (\pm 0.2)$  measured by Gadet and Pouradier (1972). However, it is clear that a mixed complex of the form  $\text{AuClOH}^-$  is unlikely to play a significant role in the transport of gold by natural ore forming fluids as the stability of such complex is low compared to single ligand complexes such as  $\text{AuCl}_2^-$  and  $\text{AuOH}(\text{aq})$ . This is demonstrated in Figure 10. At all temperatures and pressures, the  $\text{AuOH}(\text{aq})$  and  $\text{AuCl}_2^-$  complexes will predominate in chloride-containing and chloride-free aqueous solutions. Only at very alkaline pH and in very dilute acidic high temperature solutions will  $\text{Au}(\text{OH})_2^-$  and  $\text{Au}^+$  predominate but  $\text{AuClOH}^-$  was never found to contribute significantly to the total dissolved gold in solution.

Table 8. Calculated maximum solubility constant for  $\text{Au}(\text{OH})_2^-$  and maximum formation constant for  $\text{AuClOH}^-$ ; swvp denotes saturation water vapor pressure.

$t/^\circ\text{C}$	$p/\text{bar}$	$\log K_{s,002}^a$	$\log \beta_{002}^b$	$\log K_{\text{AuClOH}}^c$
25	swvp	$-26.6 \pm 1.0^d$	$22.0 \pm 1.0^d$	$15.7 \pm 0.2^d$
25	swvp	—	—	15.9
300	500	$-7.13 \pm 0.15$	$15.47 \pm 0.15$	11.2
350	500	$-6.64 \pm 0.10$	$14.77 \pm 0.10$	10.7
400	500	$-5.85 \pm 0.10$	$15.05 \pm 0.10$	10.9
450	500	$-5.41 \pm 0.10$	$14.37 \pm 0.10$	10.8
400	1000	$-6.34 \pm 0.10$	$16.79 \pm 0.10$	11.4
500	1000	$-5.97 \pm 0.10$	$12.83 \pm 0.10$	9.3
600	1000	$-5.90 \pm 0.10$	$12.94 \pm 0.10$	9.4
600	1500	$-5.90 \pm 0.10$	$11.10 \pm 0.10$	7.9

<sup>a</sup> Maximum solubility constant for the reaction  $\text{Au}(\text{s}) + \text{H}_2\text{O} + \text{OH}^- = \text{Au}(\text{OH})_2^- + 0.5\text{H}_2(\text{g})$  estimated from the experimental results of Stefánsson and Seward (2003).

<sup>b</sup> Maximum formation constant for the reaction  $\text{Au}^+ + 2\text{OH}^- = \text{Au}(\text{OH})_2^-$  calculated from the solubility constant  $K_{s,002}$ , ion product of water ( $K_w$ ) and the gold redox potential ( $K_{s,r}$ ) (Table A1).

<sup>c</sup> Formation constant for the reaction  $\text{Au}^+ + \text{Cl}^- + \text{OH}^- = \text{AuClOH}^-$ .

<sup>d</sup> Calculated from experimental results of Gadet and Pouradier (1972).

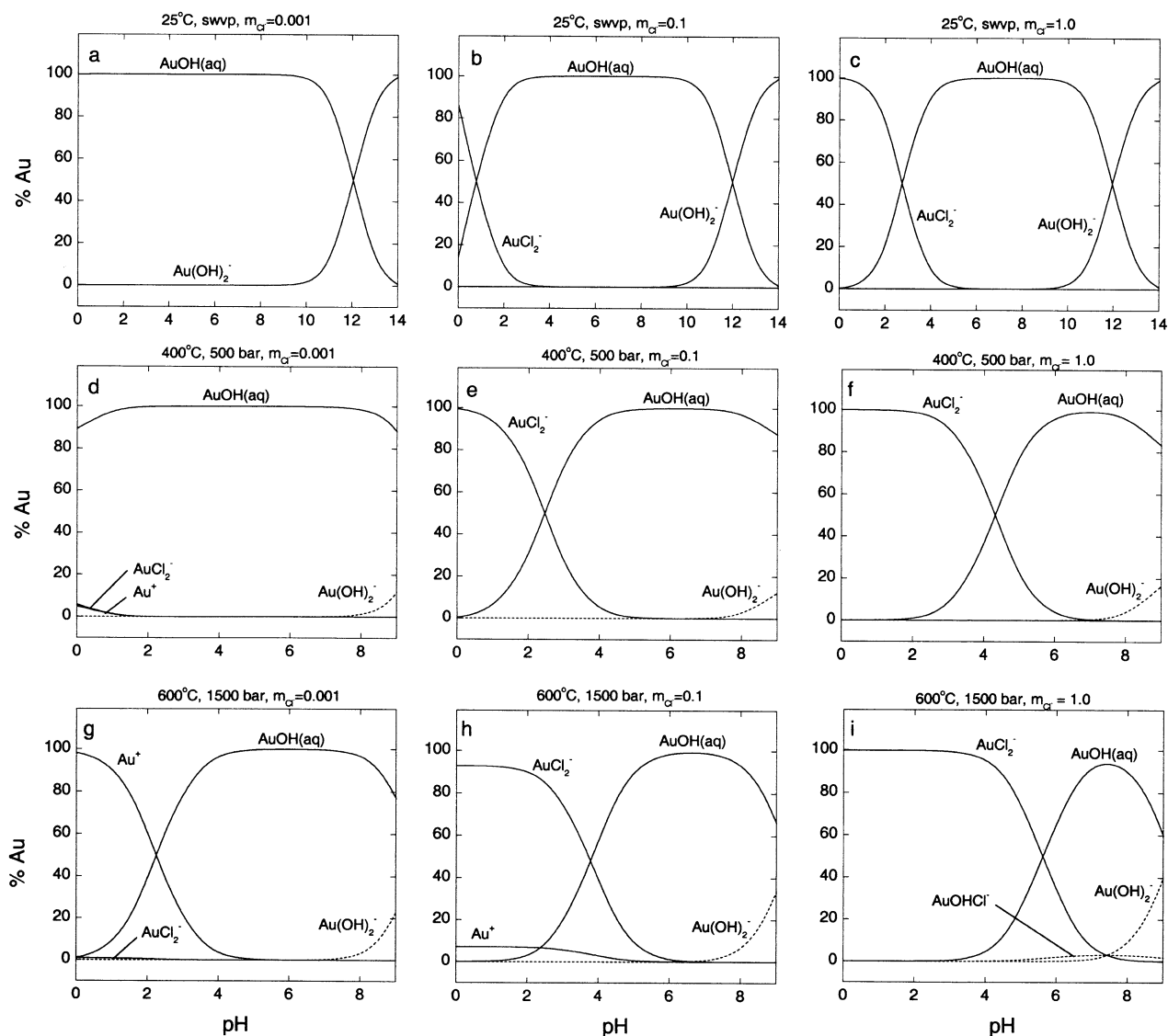


Fig. 10. Speciation diagram summarising the distribution of  $\text{Au}^+$ ,  $\text{AuOH(aq)}$ ,  $\text{Au(OH)}_2^-$ ,  $\text{AuCl}_2^-$  and  $\text{AuClOH}^-$  as a function of pH at variable chloride molality, temperature and pressure. Calculated contributions of less than 1% of the total concentration are not shown in the diagram. The dashed curves for  $\text{Au(OH)}_2^-$  and  $\text{AuClOH}^-$  represent the maximum stability of these complexes; swvp denotes saturation water vapor pressure.

#### 4.4. Comparison with Previous Results

The most extensive study on the complexation of gold(I) with chloride ligands is that of Zotov et al. (1991), who measured the solubility of gold in  $\text{HCl}+\text{KCl}$  and  $\text{HCl}+\text{NaCl}$  solutions between 350 and 500°C and between 500 and 1500 bar. The redox potential in their experiments was fixed by the addition of metallic aluminium that reacts to form  $\text{Al}_2\text{O}_3$  and  $\text{H}_2$ . Zotov et al. (1991) interpreted their results with respect to  $\text{AuCl}_2^-$  stoichiometry and gave the equilibrium solubility constant with respect to this complex. The originally reported constants for  $\text{AuCl}_2^-$  (Eqn. 22 of Zotov et al., 1991) are somewhat higher than the values obtained in this study. For their calculations, Zotov et al. (1991) used the dissociation constants of  $\text{HCl(aq)}$  of Frantz and Marshall (1984) which differ by up to

2.5 log units at  $\rho_w < 0.5 \text{ g cm}^{-3}$  from those of Ho et al. (2001) used in our study. Therefore, to compare the measured solubilities of Zotov et al. (1991) with those of our study, the solubility constant based on the results of Zotov et al. (1991) was recalculated using the same procedure and thermodynamic database as for the data of the present study (Table A1). The results are given in Table 9 and Figure 5. Despite several discrepancies (e.g., at 450°C and 500 bar), the overall agreement between our data and those of Zotov et al. (1991) (recalculated) is good (Fig. 5).

Gammons and Williams-Jones (1995) measured the solubility of Au-Ag alloy (electrum) and  $\text{AgCl}$  (chlorargyrite) at 300°C and saturation water vapor pressure. The solution pH and the chloride concentration were fixed by addition of  $\text{NaCl}$

Table 9. Comparison of the experimentally derived equilibrium solubility constant  $\log K_{s,020}$  determined in this study with literature data.

$t/^\circ\text{C}$	$p/\text{bar}$	This study	Z <sup>abd</sup>	N <sup>a</sup>	G <sup>a</sup>
25	swvp	—	—	-19.39	—
300	swvp	—	—	—	$-5.34 \pm 0.39$
300	500	$-5.43 \pm 0.29$	—	—	—
450	500	$-1.22 \pm 0.10$	$-2.26 \pm 0.12$	—	—
350	1000	—	$-4.23 \pm 0.21$	—	—
450	1000	$-2.80 \pm 0.11$	$-2.81 \pm 0.05$	—	—
450	1000	$-2.80 \pm 0.11$	$-3.03 \pm 0.12^c$	—	—
500	1000	$-1.96 \pm 0.18$	$-2.18 \pm 0.08$	—	—
450	1500	$-3.11 \pm 0.28$	$-3.12 \pm 0.10$	—	—

<sup>a</sup> Z: Zotov et al. (1991); N: Nikolaeva et al. (1972); G: Gammons and Williams-Jones (1995).

<sup>b</sup> Recalculated in the present study using the data in Appendix A.

<sup>c</sup> Measured in the system NaCl + HCl.

<sup>d</sup> Measured in KCl + HCl solutions if not otherwise indicated.

and HCl. The redox potential was controlled by varying the solution composition and by varying the electrom composition. Gammons and Williams-Jones (1995) interpreted their results in terms of  $\text{AuCl}_2^-$  and  $\text{AgCl}_2^-$  complexes and estimated the solubility constant of this gold and silver with respect to these species. The data for  $\text{AgCl}_2^-$  compare well with previous studies (Seward, 1976; Zotov et al., 1986) as does their value of  $K_{s,020}$  with that reported in this study (Fig. 5).

Wood et al. (1987) measured the solubility of the assemblage gold + pyrite + pyrrhotite + magnetite + sphalerite + galena + stibnite + argentite + bismuthinite + molybdenite in  $\text{H}_2\text{O} + \text{NaCl} + \text{CO}_2$  solutions at 200 to 350°C and saturation water vapor pressure. The total molality of the solutions ranged from 0.0 to 5.0 NaCl. A strong positive correlation was observed between the total aqueous gold concentration and the activity of chloride, suggesting the presence of a gold(I) chloride complex. However, the large scatter of their data and the overall complexity of the chemical system make conclusive determination of dominant gold(I) complex stoichiometries and stabilities impossible.

Henley (1973) measured the solubility of gold from 300 to 500°C and from 1000 to 2000 bar in 0.5–2 mol  $\text{kg}^{-1}$  KCl solutions with the redox potential and pH fixed by the mineral buffers hematite + magnetite and muscovite + quartz + K-feldspar, respectively. Henley (1973) obtained very variable and high solubilities and interpreted the solubilities in terms of dinuclear  $\text{Au}_2\text{Cl}_2(\text{aq})$  complex. Later, a number of attempts were made to reinterpret Henley's (1973) data with respect to the  $\text{AuCl}_2^-$  complex stoichiometry (e.g., Wood et al., 1987). As pointed out by Gammons and Williams-Jones (1995), there is a systematic variation in the gold solubility depending on the experimental container that in some cases clearly reacted with the solution changing its composition and aqueous species activities. Moreover, very large differences were often observed by Henley (1973) for replicate solubility measurements. These overall uncertainties and scatter make any conclusive determination of the gold complex stoichiometry and stability impossible.

The results of the present study are compared with previous results of Nikolaeva et al. (1972) and Gammons and Williams-

Jones (1995) and the recalculated solubility constant of Zotov et al. (1991) in Table 9 and Figure 5. A good agreement is observed between all studies indicating that the measured solubilities are consistent. The exact values for the solubility constant at a given temperature and pressure is, on the other hand, extremely dependent on the values of the dissociation constants employed for  $\text{HCl}(\text{aq})$  and  $\text{NaCl}(\text{aq})$  or  $\text{KCl}(\text{aq})$  and  $\text{NaOH}(\text{aq})$  or  $\text{KOH}(\text{aq})$ . We further note that some of the ion pair constants within the SUPCRT92 database (Johnson et al., 1992) are spurious at high temperatures and pressures. Using these data to derive equilibrium constants for  $\text{AuCl}_2^-$  from our solubility data will lead to values of the constants that differ from those presented here by 0.6 to 3.0 log units.

## 5. CONCLUSIONS

The solubility of gold was measured in the system  $\text{H}_2\text{O} + \text{H}_2 + \text{HCl} + \text{NaCl} + \text{NaOH}$  at temperatures between 300 and 600°C and pressures of 500 to 1800 bar. They were found to be in the range  $9.9 \times 10^{-9}$  to  $3.26 \times 10^{-5}$  mol  $\text{kg}^{-1}$  total dissolved gold, in solutions of total chloride between 0.150 and 1.720 mol  $\text{kg}^{-1}$ , total dissolved sodium between 0.000 and 0.975 mol  $\text{kg}^{-1}$ , total dissolved hydrogen between  $4.34 \times 10^{-6}$  and  $7.87 \times 10^{-4}$  mol  $\text{kg}^{-1}$  and a corresponding  $\text{pH}_{T,p}$  of 0.6 to 11.2. A nonlinear least squares treatment of the data demonstrates that the  $\text{AuCl}_2^-$  is the only detectable chloride complex in solution over a wide range of temperature and pressure. The equilibrium solubility constant  $\log K_{s,020}$  for the formation of  $\text{AuCl}_2^-$  was found to increase with increasing temperature and decrease with increasing pressure. The solubility of gold at  $\text{pH} > 5$  was found to be independent of chloride concentration up to 1 mol  $\text{kg}^{-1}$  and identical to the solubility of gold with respect to  $\text{AuOH}(\text{aq})$  as determined by Stefánsson and Seward (2003). The results indicate that a mixed chloridohydroxygold(I) complex,  $\text{AuClOH}^-$ , is three to six orders of magnitude less stable than  $\text{AuOH}(\text{aq})$  and  $\text{AuCl}_2^-$  in hydrothermal solutions. It is concluded that gold(I) chloride complexes play an important role in gold transport in acidic chloride-rich hydrothermal solutions above 400°C.

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## APPENDIX

Table A1. The logarithm of the equilibrium constants used in this study for the aqueous speciation calculations.

Reaction	p/bar	t/°C							Ref.
		300	350	400	450	500	550	600	
$\text{H}_2\text{O}(l) = \text{H}^+ + \text{OH}^-$	500	-10.86	-11.14	-11.88	-13.74	-16.13			a
	1000	-10.50	-10.54	-10.77	-11.19	-11.81	-12.60	-13.40	a
	1500	-10.26	-10.22	-10.29	-10.48	-10.77	-11.15	-11.59	a
	1800	-10.12	-10.05	-10.08	-10.20	-10.41	-10.68	-11.00	a
$\text{HCl}(\text{aq}) = \text{H}^+ + \text{Cl}^-$	500	-0.98	-1.64	-2.54	-4.13	-6.03			b
	1000	-0.76	-1.27	-1.83	-2.46	-3.19	-3.99	-4.78	b
	1500	-0.59	-1.05	-1.51	-1.99	-2.50	-3.03	-3.57	b
	1800	-0.51	-0.95	-1.37	-1.81	-2.26	-2.71	-3.18	b
$\text{H}_2(\text{g}) = \text{H}_2(\text{aq})$	500	-2.66	-2.32	-1.90	-1.42	-0.95			c
	1000	-2.90	-2.65	-2.38	-2.08	-1.77	-1.47	-1.19	c
	1500	-3.08	-2.87	-2.61	-2.34	-2.05	-1.76	-1.51	c
	1800	-3.19	-2.98	-2.74	-2.47	-2.19	-1.91	-1.66	c
$\text{NaOH}(\text{aq}) = \text{Na}^+ + \text{OH}^-$	500	-1.17	-1.54	-2.05	-2.94	-4.08			d
	1000	-1.09	-1.39	-1.72	-2.11	-2.58	-3.11	-3.66	d
	1500	-1.03	-1.30	-1.58	-1.88	-2.21	-2.57	-2.95	d
	1800	-1.00	-1.26	-1.52	-1.79	-2.08	-2.40	-2.72	d
$\text{NaCl}(\text{aq}) = \text{Na}^+ + \text{Cl}^-$	500	-0.51	-0.95	-1.59	-2.80	-4.32			e
	1000	-0.36	-0.69	-1.08	-1.54	-2.11	-2.76	-3.43	e
	1500	-0.26	-0.54	-0.85	-1.19	-1.57	-1.99	-2.44	e
	1800	-0.20	-0.47	-0.75	-1.05	-1.39	-1.74	-2.12	e
$\text{Au}(s) + \text{H}^+ = \text{Au}^+ + 0.5\text{H}_2(\text{g})$	500	-11.74	-10.27	-9.02	-7.94	-7.00			f
	1000	-11.75	-10.27	-9.01	-7.94	-6.99	-6.17	-5.44	f
	1500	-11.76	-10.27	-9.01	-7.93	-6.98	-6.15	-5.41	f
	1800	-11.75	-10.27	-9.02	-7.93	-6.99	-6.16	-5.42	f

<sup>a</sup>Marshall and Franck (1981).<sup>b</sup>Ho et al (2001).<sup>c</sup>See text.<sup>d</sup>Ho and Palmer (1996).<sup>e</sup>Ho et al. (1994).<sup>f</sup>SUPCRT92, Johnson et al. (1992).

Table A2. Experimental results.

$p/\text{bar}$	$m_{\text{HCl}}/\text{mol kg}^{-1}$	$m_{\text{NaCl}}/\text{mol kg}^{-1}$	$m_{\text{NaOH}}/\text{mol kg}^{-1}$	$m_{\text{H}_2(\text{aq})}/\text{mol kg}^{-1}$	$m_{\text{Au}}/\text{mol kg}^{-1}$
$t = 300^\circ\text{C}$					
500	0.309	0.104		3.79E-05	4.34E-07
500	0.309	0.104		3.78E-05	3.04E-07
500	0.586	0.135		3.67E-05	3.65E-07
500	0.586	0.135		4.34E-06	1.38E-06
500	0.586	0.135		4.37E-06	1.44E-06
500	0.586	0.135		3.67E-05	3.98E-07
500	0.162	0.153		3.81E-05	2.73E-07
500	0.162	0.153		3.81E-05	3.32E-07
500	0.162	0.153		3.79E-05	5.6E-08
500	0.162	0.153		3.80E-05	2.04E-07
500	0.162	0.153		3.79E-05	1.15E-07
500	0.162	0.153		3.79E-05	9.0E-08
500	0.162	0.153		3.79E-05	1.12E-07
500	0.162	0.153		3.79E-05	7.5E-08
500	0.162	0.153		3.79E-05	9.3E-08
500	0.162	0.153		3.79E-05	9.2E-08
500	0.162	0.153		3.80E-05	1.31E-07
500	0.162	0.153		3.80E-05	1.45E-07
500	0.162	0.153		3.80E-05	1.44E-07
500	0.162	0.153		3.80E-05	1.27E-07
500		0.150		3.87E-05	2.0E-08
500		0.150		3.86E-05	2.0E-08
500		0.499		3.66E-05	9.9E-09
500		0.510	0.105	3.62E-05	2.8E-08
500		0.510	0.105	3.62E-05	4.0E-08
500		0.518	0.298	3.56E-05	3.8E-08
500		0.518	0.298	3.56E-05	4.1E-08
500	0.005	0.507		3.65E-05	6.3E-08
500	0.005	0.507		3.65E-05	4.9E-08
500	0.470			3.76E-05	1.02E-07
$t = 350^\circ\text{C}$					
500	0.98			4.24E-05	2.67E-06
500	0.98			4.29E-05	3.47E-06
500	1.72			4.77E-05	9.02E-06
500	1.72			4.75E-05	7.75E-06
500	0.309	0.104		3.88E-05	7.54E-07
500	0.309	0.104		3.88E-05	8.26E-07
500	0.309	0.104		7.64E-04	1.81E-07
500	0.309	0.104		7.64E-04	1.93E-07
500	0.586	0.135		3.98E-05	3.00E-06
500	0.586	0.135		3.96E-05	2.72E-06
500	0.586	0.135		7.51E-04	6.28E-07
500	0.586	0.135		7.51E-04	6.21E-07
500	0.162	0.153		3.85E-05	2.61E-07
500	0.162	0.153		3.85E-05	2.88E-07
500		0.150		3.88E-05	1.33E-07
500		0.150		3.88E-05	8.8E-08
500		0.499		3.70E-05	1.38E-07
500		0.975		3.47E-05	5.5E-08
500		0.975		3.48E-05	1.84E-07
500		0.510	0.105	3.70E-05	5.56E-07
500		0.510	0.105	3.68E-05	3.11E-07
500		0.518	0.298	3.61E-05	7.0E-08
500		0.518	0.298	3.61E-05	5.5E-08
500	0.005	0.507		3.70E-05	2.16E-07
500	0.470			3.84E-05	7.54E-07
$t = 400^\circ\text{C}$					
500	0.98			4.24E-05	8.53E-06
500	0.98			4.29E-05	9.41E-06
500	1.72			4.77E-05	1.91E-05
500	1.72			4.75E-05	1.86E-05
500	0.309	0.104		4.06E-05	3.61E-06
500	0.309	0.104		4.05E-05	3.47E-06
500	0.309	0.104		7.76E-04	7.46E-07
500	0.309	0.104		7.76E-04	7.21E-07
500	0.586	0.135		4.18E-05	6.65E-06



Table A2. continued

$p/\text{bar}$	$m_{\text{HCl}}/\text{mol kg}^{-1}$	$m_{\text{NaCl}}/\text{mol kg}^{-1}$	$m_{\text{NaOH}}/\text{mol kg}^{-1}$	$m_{\text{H}_2}(\text{aq})/\text{mol kg}^{-1}$	$m_{\text{Au}}/\text{mol kg}^{-1}$
500	0.586	0.135		4.17E-05	6.44E-06
500	0.586	0.135		7.69E-04	1.55E-06
500	0.586	0.135		7.69E-04	1.43E-06
500	0.162	0.153		3.95E-05	1.68E-06
500	0.162	0.153		3.95E-05	1.55E-06
500	1.00E-09	0.150		3.90E-05	2.84E-07
500	1.00E-09	0.150		3.90E-05	3.33E-07
500	1.00E-09	0.499		3.76E-05	4.96E-07
500	1.00E-09	0.499		3.75E-05	2.89E-07
500	1.00E-09	0.975		3.57E-05	1.12E-06
500		0.510	0.105	3.71E-05	2.64E-07
500		0.510	0.105	3.72E-05	4.44E-07
500	0.005	0.507		3.75E-05	5.45E-07
500	0.005	0.507		3.76E-05	5.68E-07
500	0.470			3.98E-05	1.52E-06
500	0.470			4.03E-05	2.54E-06
500	0.470			4.06E-05	6.05E-06
1000	1.400			5.77E-05	1.06E-05
1000	1.400			6.24E-05	8.01E-06
1500	1.400			6.78E-05	1.21E-05
1500	1.400			6.26E-05	7.18E-06
1800	1.400			5.77E-05	1.17E-05
1800	1.400			5.77E-05	8.58E-06
$t = 450^\circ\text{C}$					
500	0.309	0.104		4.05E-05	2.32E-06
500	0.309	0.104		4.05E-05	2.30E-06
500	0.309	0.104		7.87E-04	4.80E-07
500	0.309	0.104		7.87E-04	4.64E-07
500	0.586	0.135		4.13E-05	4.14E-06
500	0.586	0.135		4.12E-05	4.01E-06
500	0.586	0.135		7.85E-04	9.65E-07
500	0.586	0.135		7.85E-04	8.88E-07
500	0.162	0.153		4.03E-05	2.15E-06
500	0.162	0.153		3.97E-05	8.67E-07
500		0.150		3.95E-05	5.30E-07
500		0.150		3.95E-05	5.08E-07
500		0.499		3.83E-05	5.08E-07
500		0.499		3.84E-05	6.51E-07
500		0.975		3.52E-05	6.88E-07
500		0.975		3.59E-05	2.14E-06
500		0.510	0.105	3.78E-05	3.92E-07
500	0.005	0.507		3.82E-05	4.11E-07
500	0.005	0.507		3.82E-05	3.19E-07
500	0.470			4.04E-05	1.78E-06
1000	1.400			6.02E-05	9.26E-06
1000	1.400			6.08E-05	1.34E-05
1500	1.400			6.79E-05	3.26E-05
1500	1.400			6.33E-05	1.34E-05
1800	1.400			5.92E-05	1.46E-05
1800	1.400			5.92E-05	2.36E-05
$t = 500^\circ\text{C}$					
500	0.309	0.104		4.00E-05	1.16E-06
500	0.309	0.104		4.00E-05	1.15E-06
500	0.586	0.135		4.03E-05	1.98E-06
500	0.586	0.135		4.03E-05	1.92E-06
500	0.162	0.153		3.99E-05	7.74E-07
500	0.162	0.153		3.99E-05	7.85E-07
500	0.470			4.07E-05	2.08E-06
500	0.470			4.06E-05	2.03E-06
1000	1.400			8.26E-05	8.83E-06
1000	1.400			7.98E-05	4.42E-06
1000	0.980			8.04E-05	5.21E-06
1000	0.980			7.99E-05	3.87E-06
1500	1.400			8.11E-05	1.23E-05
1500	1.400			8.73E-05	2.06E-05
1500	0.980			8.12E-05	9.50E-06

Table A2. continued

$p/\text{bar}$	$m_{\text{HCl}}/\text{mol kg}^{-1}$	$m_{\text{NaCl}}/\text{mol kg}^{-1}$	$m_{\text{NaOH}}/\text{mol kg}^{-1}$	$m_{\text{H}_2}(\text{aq})/\text{mol kg}^{-1}$	$m_{\text{Au}}/\text{mol kg}^{-1}$
1500	0.980			8.08E-05	9.83E-06
1800	1.400			6.23E-05	1.50E-05
1800	1.400			6.63E-05	1.79E-05
$t = 550^\circ\text{C}$					
1000	1.400			6.34E-05	8.60E-06
1000	1.400			6.23E-05	6.40E-06
1000	0.980			6.13E-05	6.02E-06
1000	0.980			6.02E-05	4.33E-06
1500	1.400			6.44E-05	1.20E-05
1500	1.400			6.92E-05	1.05E-05
1500	0.980			6.29E-05	8.52E-06
1500	0.980			6.26E-05	8.87E-06
1800	1.400			6.12E-05	1.30E-05
1800	1.400			6.12E-05	2.20E-05
$t = 600^\circ\text{C}$					
1000	1.400			8.30E-05	6.48E-06
1000	1.400			8.20E-05	6.24E-06
1000	0.980			8.22E-05	2.18E-06
1000	0.980			8.13E-05	2.01E-06
1500	1.400			8.28E-05	1.26E-05
1500	1.400			8.23E-05	1.73E-05
1500	0.980			8.17E-05	6.81E-06
1500	0.980			8.19E-05	6.20E-06
1800	1.400			6.18E-05	1.40E-05
1800	1.400			6.18E-05	8.00E-06