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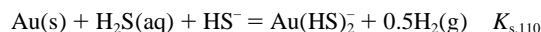
Gold(I) complexing in aqueous sulphide solutions to 500°C at 500 bar

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Abstract—The solubility of gold has been measured in aqueous sulphide solutions from 100 to 500°C at 500 bar in order to determine the stability and stoichiometry of sulphide complexes of gold(I) in hydrothermal solutions. The experiments were carried out in a flow-through system. The solubilities, measured as total dissolved gold, were in the range 3.6×10^{-8} to 6.65×10^{-4} mol kg⁻¹ (0.007–131 mg kg⁻¹), in solutions of total reduced sulphur between 0.0164 and 0.133 mol kg⁻¹, total chloride between 0.000 and 0.240 mol kg⁻¹, total sodium between 0.000 and 0.200 mol kg⁻¹, total dissolved hydrogen between 1.63×10^{-5} and 5.43×10^{-4} mol kg⁻¹ and a corresponding pH_{T, p} of 1.5 to 9.8. A non-linear least squares treatment of the data demonstrates that the solubility of gold in aqueous sulphide solutions is accurately described by the reactions



where AuHS(aq) is the dominant species in acidic solutions and Au(HS)₂⁻ under neutral pH conditions. With increasing temperature, the stability field of Au(HS)₂⁻ shifts to more alkaline pH in accordance with the shift of the first ionisation constant of H₂S(aq). In addition, AuOH(aq) was found to be an important species in acidic solutions at *t* > 400°C. The equilibrium solubility constant to form AuHS(aq) was found to increase from log *K*_{s,100} = -6.20 ± 0.11 at 200°C to maximum of -5.63 ± 0.07 to 0.11 at 350°C and then decrease to -6.25 ± 0.19 at 500°C. The solubility constant to form Au(HS)₂⁻ increases with increasing temperature from log *K*_{s,110} = -2.33 ± 0.14 at 100°C to -1.27 ± 0.07 at 250°C and then decrease to -1.73 ± 0.25 at 500°C. From these measurements, the equilibrium stepwise and cumulative formation constants were calculated. The complex formation at 25°C is characterised by an exothermic enthalpy and small positive entropy, both of which are consistent with the predominantly covalent interaction between Au⁺ and HS⁻. With increasing temperature, the cumulative formation reactions become endothermic and are accompanied with large positive entropy of reaction, indicating greater electrostatic interaction. The aqueous speciation of gold(I) is very sensitive to fluid composition and temperature. In low-temperature geothermal fluids, gold(I) sulphide complexes predominate whereas at higher temperatures, gold(I) hydroxide and chloride complexes may also play a role in hydrothermal gold transport in the Earth's crust. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

A knowledge of the stability of aqueous gold(I) complexes in hydrothermal solutions is essential for quantitative interpretation of the transport and depositional mechanisms of gold by hydrothermal fluids in the Earth's crust. It is generally accepted that gold is predominantly transported as chloride and sulphide complexes in natural hydrothermal solutions and previous experimental studies have mainly focused on the complexing of gold(I) with chloride ligands (Nikolaeva et al., 1972; Henley, 1973; Wood et al., 1987; Zotov et al., 1991; Gammons and Williams-Jones, 1995; Frank et al., 2002; Stefánsson and Seward, 2003b) and sulphide ligands (Seward, 1973; Belevantsev et al., 1981; Renders and Seward, 1989; Shenberger and Barnes, 1989; Hayashi and Ohmoto, 1991; Pan and Wood, 1994; Benning and Seward, 1996; Zotov et al., 1996; Baranova and Zotov, 1998; Gibert et al., 1998; Loucks and Mavrogenes, 1999). The gold(I) sulphide complexes are much more stable than gold(I) chloride complexes by about twenty orders of magnitude at 25°C and are also thought to predominate in most

natural geothermal fluids (Seward, 1991). Nevertheless, the stability and stoichiometry of gold(I) sulphide complexes are a matter of some controversy, especially at higher temperatures where there are significant discrepancies amongst the various sets of data reported in the literature.

The aim of this study was thus to determine the stability and stoichiometry of gold(I) sulphide complexes at high temperatures by measuring the solubility of gold in dilute sulphide solutions in such a way as to eliminate and/or minimise possible sources of error inherent in many of the previous reported studies. For this purpose, a flow-through system was designed and constructed, which made it possible to measure independently the concentrations of all components of importance in the system without disturbing the chemical equilibrium. Moreover, by measuring the concentrations of all the relevant components, the possible loss of hydrogen and hydrogen sulphide could be identified and subsequently avoided. Previously, the stability of gold(I) hydroxide and chloride complexes in hydrothermal solutions have been measured in our laboratory (Stefánsson and Seward, 2003a, 2003b) and these measurements make it possible to determine the stability of gold(I) sulphide complexes from solubility measurements in the sys-

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tem $\text{H}_2\text{O} + \text{H}_2 + \text{H}_2\text{S} + \text{HCl} + \text{NaOH}$. The intention has also been to provide an internally consistent and accurate thermodynamic data base pertaining to complexes of gold(I) with HS^- , Cl^- and OH^- at high temperatures and pressures to enable the modelling of the transport and deposition of gold by fluids in the Earth's crust.

2. EXPERIMENTAL PROCEDURES

The solubility measurements were carried out using a flow-through autoclave system (Fig. 1). The low-pressure part of the system was made of Pyrex glass, PEEK tubing and Teflon. All the wetted, high-pressure parts were made of titanium and gold. The solubility experiments were carried out in a gold-lined (99.99%) autoclave filled with pure gold "sand." The total surface area of gold "sand" through which the solutions were pumped was $\sim 1 \text{ m}^2$. During the experiments no changes were observed in the properties and the size of the gold "sand." Initially, the experiments were carried out in an autoclave made of RMI 0.2% Pd-titanium alloy. Before use, the titanium tubes and the autoclave were heated for 24 h at 400°C , then rinsed with 65% HNO_3 (Merck Suprapur) following several washes with deionised water. In this way, a relatively inert corrosion resistant titanium oxide layer was produced. However, problems were encountered involving interaction of hydrogen with the titanium autoclave. A discussion of these results has been included to emphasise the experimental difficulties involving hydrogen and the experimental study of redox reactions in hydrothermal solutions. All the equilibrium solubility experi-

ments reported here were carried out in the gold-lined, flow-through autoclave.

The gold-lined autoclave was placed in a large volume Carbolite oven, the temperature of which was controlled to within $\pm 0.5^\circ\text{C}$. The temperature was monitored by three thermocouples at the inlet and the outlet of the autoclave. These temperatures never differed by $>1^\circ\text{C}$ from the stated temperature and were usually within 0.5°C . The pressure was generated by an HPLC pump and measured using a titanium pressure transducer in the pressure module of the pump itself and using a pressure gauge connected to the outflow end of the back pressure regulator. The two readings were never found to deviate from the set pressure by $>5 \text{ bar}$. The pump supplied the inlet solution to the line and the flow rate of the solution was maintained constant, typically at $<1 \text{ mL min}^{-1}$ but could be varied from 0.01 to 10 mL min^{-1} .

All the reagents used in the experiments and for chemical analysis were Merck Suprapur and pro analyse grade. The solutions used in the experiments were prepared from deionised, double distilled water (in quartz glass), 50% NaOH solution and deoxygenated 30% HCl. To exclude oxygen, the solutions were boiled under vacuum in an ultrasonic bath and then oxygen free argon gas was bubbled through, this procedure being repeated several times. Reduced sulphur and hydrogen were added to the deoxygenated solution by passing H_2S - H_2 -Ar gas mixture through it at 20°C and $1.2 \pm 0.2 \text{ bar}$. The gas mixtures were prepared using an Enviro-nics computer interfaced gas mixer from pure or mixtures of H_2S (grade 2.0), H_2 (grade 2.0) and deoxygenated Ar (grade 4.8). Deoxygenated

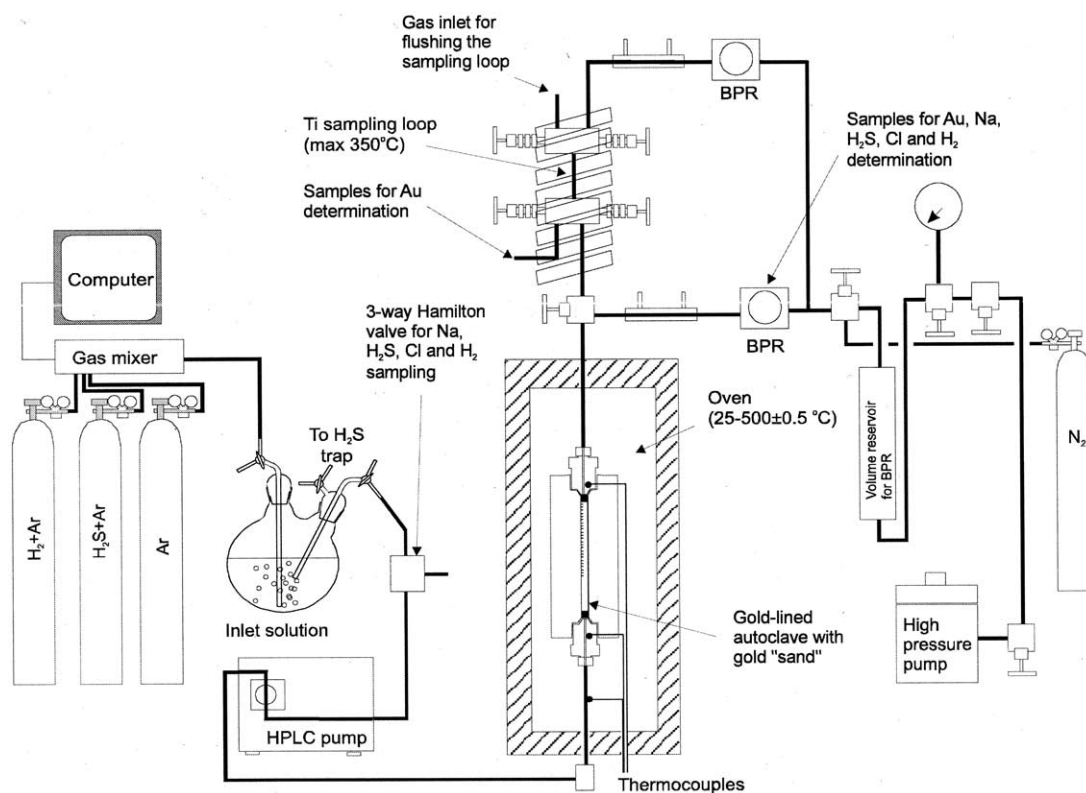


Fig. 1. A schematic diagram of the apparatus designed and used in the present study; BPR: back pressure regulator.

30% HCl was added to the respective solution using a gas-tight Hamilton valve and syringe where appropriate.

Liquid sampling was carried out at three positions. Firstly, the outgoing tube from the autoclave was connected to a titanium sampling loop that could be kept at experimental temperature and pressure. The titanium sampling loop was used to check for gold loss upon cooling and depressurisation and has been previously described in details by Stefánsson and Seward (2003c). Secondly, samples were collected from the outflow (low pressure end) of the back-pressure regulator. Thirdly, samples were collected directly from the inlet solution flask using a gas-tight Hamilton three-way valve. Samples for the determination of dissolved gold, sulphide, sodium and chloride were collected in polypropylene syringes and samples for determination of dissolved hydrogen were collected using preevacuated gas bottles with gas-tight Teflon stopcocks.

The samples for gold analyses were added to an acid washed Pyrex flask and weighed. before analysis, the samples were treated by three different methods to minimise possible back-reactions, preconcentrate the gold in solution and eliminate interferences. In the first method, the samples were boiled down to dryness, the residue dissolved in 1.5 mL of aqua regia, then evaporated to near dryness on a water bath and re-diluted with 6% HCl. The second method involved the addition of 0.5 mL of 25% NH₃ followed by ~1 mL of 30% H₂O₂ to the sample to oxidise the H₂S to SO₄. The solutions were taken up in 6% HCl. With the third method, the gold was extracted into 5 mL of methyl-isobutyl-ketone (MIBK) to eliminate sodium interference. After shaking for >5 min the MIBK solvent was separated for analysis by a flame atomic absorption spectrometry (FAAS) using a Varian 840A spectrometer. Standard solutions were matrix-matched and prepared in the same way as the samples. The precision and the detection limit of the analyses were found to vary according to the method used and the total dissolved gold concentration.

For the aqua regia method, the dissolved gold could be concentrated by up to 30 times decreasing the detection limits to ~2 × 10⁻⁸ mol kg⁻¹. The precision of the analysis was found to be 3% and 3 × 10⁻⁸ mol kg⁻¹ above and below 5 × 10⁻⁷ mol kg⁻¹ at the 95% confidence level, respectively. For the NH₃-H₂O₂ method no preconcentration could be carried out and the detection limit was 5.0 × 10⁻⁷ mol kg⁻¹ and the precision of the analysis was 6% at the 95% confidence level. For the MIBK method, the samples could be concentrated up to 20 times by varying the sample to MIBK ratio. Also, the effect of sodium interference was eliminated. The precision of the method down to $m_{Au} = 5.0 \times 10^{-8}$ mol kg⁻¹ was 3% at the 95% confidence level. The MIBK method was preferred at low gold concentrations and high sodium concentration. Results for gold by all methods were in good agreement within uncertainties.

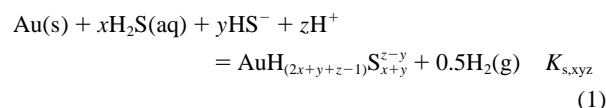
Total reduced sulphur was measured by iodometric back titration with a precision of 3% at the 95% confidence level. Total sodium was determined by flame atomic emission spectrometry. The precision of the analyses was found to be 3% at the 95% confidence level. Total chloride was determined gravimetrically after precipitation with standardised 0.10 mol/L AgNO₃ solution. before addition of AgNO₃, H₂O₂ was added to oxidise H₂S to SO₄. The precision of the analyses was found to be 2% at the 95% confidence level.

Preevacuated gas bottles with gas-tight Teflon stopcocks were used for the collection of samples for hydrogen determination. An appropriate amount of 0.25 mol/L cadmium acetate and 4 mol/L NaOH solution was added to the bottle before evacuation to adsorb all the H₂S from the gas phase. The gas composition was measured at isothermal conditions of 50°C using a gas chromatograph. A 30-m-long column containing a 5-Å mesh size molecular sieve was used with nitrogen as the carrier gas. In this way, the partial pressures of hydrogen and argon in the gas phase could be separated and determined. 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 as well as the Ar/H₂ ratio in the experimental solutions. The precision of the analysis based on replicated samples was 2% at the 95% confidence level.

3. AQUEOUS SPECIATION

3.1. Speciation Calculations

The dissolution of gold in aqueous reduced sulphide solution forming gold(I) sulphide complexes can be expressed by the general reaction



and the corresponding solubility constant is

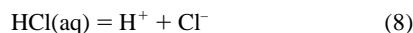
$$K_{s,xyz} = \frac{a_{\text{AuH}_{(2x+y+z-1)}\text{S}_{x+y}^{z-y}} f_{\text{H}_2(\text{g})}^{0.5}}{a_{\text{H}_2\text{S(aq)}}^x a_{\text{HS}^-}^y a_{\text{H}^+}^z} \quad (2)$$

Gold dissolves to form AuCl₂⁻ and AuOH(aq) in reduced chloride solutions at acid to alkaline pH whereas the free Au⁺ ion is unimportant (Stefánsson and Seward, 2003a, 2003b). Consequently, the total concentration of gold in reduced aqueous solution in the presence of sulphide and chloride ligands is given by

$$m_{\text{Au,total}} = \sum_x \sum_y \sum_z m_{\text{AuH}_{(2x+y+z-1)}\text{S}_{x+y}^{z-y}} + m_{\text{AuOH(aq)}} + m_{\text{AuCl}_2^-} \quad (3)$$

Experiments were carried out in the system: Au(s)+H₂+H₂O+H₂S+HCl+NaOH. In the data treatment, the following species were considered: H⁺, OH⁻, Na⁺, Cl⁻, H₂S(aq), HS⁻, NaOH(aq), NaHS(aq), HCl(aq), H₂(aq) and H₂(g) in addition to the given speciation model for gold(I) complexes as defined by Eqn. 2 and 3. The NaCl(aq) ion pair was not included in the speciation calculations as Na⁺ and Cl⁻ were never present together in any experimental run. The following independent reactions can be written for these aqueous species:





For these equilibrium reactions the following equilibrium constants can be written:

$$K_w = m_{\text{H}^+} \gamma_{\text{H}^+} m_{\text{OH}^-} \gamma_{\text{OH}^-} a_{\text{H}_2\text{O}}^{-1} \quad (10)$$

$$K_{1,\text{H}_2\text{S}} = m_{\text{H}^+} \gamma_{\text{H}^+} m_{\text{HS}^-} \gamma_{\text{HS}^-} m_{\text{H}_2\text{S}(\text{aq})}^{-1} \gamma_{\text{H}_2\text{S}(\text{aq})}^{-1} \quad (11)$$

$$K_{\text{NaOH}} = m_{\text{Na}^+} \gamma_{\text{Na}^+} m_{\text{OH}^-} \gamma_{\text{OH}^-} m_{\text{NaOH}(\text{aq})}^{-1} \gamma_{\text{NaOH}(\text{aq})}^{-1} \quad (12)$$

$$K_{\text{NaHS}} = m_{\text{Na}^+} \gamma_{\text{Na}^+} m_{\text{HS}^-} \gamma_{\text{HS}^-} m_{\text{NaHS}(\text{aq})}^{-1} \gamma_{\text{NaHS}(\text{aq})}^{-1} \quad (13)$$

$$K_{\text{HCl}} = m_{\text{H}^+} \gamma_{\text{H}^+} m_{\text{Cl}^-} \gamma_{\text{Cl}^-} m_{\text{HCl}(\text{aq})}^{-1} \gamma_{\text{HCl}(\text{aq})}^{-1} \quad (14)$$

$$K_{\text{H}} = m_{\text{H}_2(\text{aq})} \gamma_{\text{H}_2(\text{aq})} f_{\text{H}_2(\text{g})}^{-1} \quad (15)$$

The solution equilibria are also constrained by the charge balance

$$m_{\text{H}^+} + m_{\text{Na}^+} - m_{\text{OH}^-} - m_{\text{Cl}^-} - m_{\text{AuCl}_2^-} + \sum_x \sum_y \sum_z (z - y) m_{\text{AuH}_{(2x+y+z-1)}\text{S}_{x+y}^{z-y}} = 0 \quad (16)$$

and the mass balance equations

$$m_{\text{Na},\text{total}} = m_{\text{Na}^+} + m_{\text{NaOH}(\text{aq})} + m_{\text{NaHS}(\text{aq})} \quad (17)$$

$$m_{\text{Cl},\text{total}} = m_{\text{Cl}^-} + m_{\text{HCl}(\text{aq})} + 2m_{\text{AuCl}_2^-} \quad (18)$$

$$m_{\text{S},\text{total}} = m_{\text{H}_2\text{S}(\text{aq})} + m_{\text{HS}^-} + m_{\text{NaHS}(\text{aq})} + \sum_x \sum_y \sum_z (x + y) m_{\text{AuH}_{(2x+y+z-1)}\text{S}_{x+y}^{z-y}} \quad (19)$$

as well as the equilibrium constants and mass balance equation for aqueous gold (Eqn. 2 and 3) and the proton and the $\text{H}_2(\text{aq})$ mass balance equations.

The solution ionic strength varied between $I = 8.3 \times 10^{-8}$ and 0.23 mol kg^{-1} but was generally $< 0.02 \text{ mol kg}^{-1}$. Under these conditions, the activity of water was taken as unity as were the activity coefficients for the neutral aqueous species. Individual ion activity coefficients were estimated using a modified Debye-Hückel equation (Robinson and Stokes, 1968) of the form

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + a_i B \sqrt{I}} + \Gamma_\gamma + b_\gamma I \quad (20)$$

where A and B are Debye-Hückel parameters, z is the ionic charge, a is the ion size parameter taken to be 9, 4, 3.5, 3.5, 4 and 4 Å for H^+ , Na^+ , OH^- , HS^- , Cl^- and gold complexes, respectively (Kielland, 1937), Γ_γ is a mole fraction to molality conversion factor, b_γ is an empirical correction factor and I is the ionic strength. In all cases, the activity coefficients are entirely determined by the Debye-Hückel equation with the contribution from the extended term $b_\gamma I$ being negligible. The same Debye-Hückel equation was used for calculations of gold(I) chloride and hydroxide complex stabilities (Stefánsson and Seward, 2003a, 2003b) making these thermodynamic data consistent with the present study.

The aqueous speciation calculations and the determination of the solubility constants for gold were carried out simulta-

neously at a given temperature and pressure with the aid of the FITEQL computer program (Westall, 1982a, 1982b). A subroutine was added to the program for calculation of ionic strength and individual ion activity coefficients according to Eqn. 20. The calculation procedure to obtain individual aqueous species' activities and the equilibrium constants for the formation of gold(I) complexes was as follows: (1) the aqueous speciation was obtained by solving the equilibrium reactions and the mass balance equations for a given gold(I) speciation model in an iterative manner using a Newton-Raphson algorithm; the equilibrium constants used for the calculations are given in Appendix A; in addition, initial guesses for the unknown gold(I) sulphide equilibrium solubility constants were introduced; (2) from the calculated ion molalities, the ionic strength and individual activity coefficients were calculated; (3) a new estimate of the gold solubility constant was made using a nonlinear least square procedure; (4) the new solubility constants and activity coefficients were then used to recalculate the aqueous speciation and subsequently new estimates for the solubility constants for gold were made. Further repetitions of the procedure were continued until changes in the ionic strength and gold solubility constants were negligible.

The dissolved hydrogen concentration of the solution was calculated from

$$m_{\text{H}_2(\text{aq})} = K_{\text{H}} p_{\text{total}} X_{\text{H}_2(\text{g})} \quad (21)$$

where K_{H} is the Henry's law constant for hydrogen in water at 20°C calculated at the solution ionic strength (Crozier and Yamamoto, 1974), p_{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 also corrected for the contribution arising from the dissolution of gold. Moreover the total dissolved hydrogen molality $m_{\text{H}_2(\text{aq})}$ was measured on a gas chromatograph. From the dissolved hydrogen concentrations, measured or calculated, 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.

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

$$V = \frac{\sum \left(\frac{m_{\text{Au}}^{\text{exp}} - m_{\text{Au}}^{\text{calc}}}{s} \right)^2}{n_p n_{\text{II}} - n_u} \quad (22)$$

where $m_{\text{Au}}^{\text{exp}}$ is the measured gold concentration, $m_{\text{Au}}^{\text{calc}}$ is the modeled gold concentration, s is the estimated experimental error, n_p is the total number of data points, n_{II} is the number of components for which both total and free components are known, 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. Equilibrium Constants

The thermodynamic data used for the speciation calculations are given in Appendix A and the equilibrium constants calcu-

lated in this study are only consistent with these data. The ion product for water (Eqn. 10) was taken from Marshall and Franck (1981) who fitted available experimental data to a density function, which is considered reliable to 1000°C and 10 kbar. The data of Ho and Palmer (1996) for the dissociation constant for NaOH(aq) (Eqn. 12) were selected and are based on conductivity measurements of dilute sodium hydroxide solutions at high temperatures and pressures. For the dissociation constant of HCl(aq) (Eqn. 14), the recent data of Ho et al. (2001) were selected. These are based on conductivity measurements of dilute aqueous HCl solutions at high temperatures and pressures using a flow-through cell. The dissociation constant of NaHS(aq) (Eqn. 13) was assumed to be equivalent to that of NaCl(aq) measured by Ho et al. (1994) except at $t \geq 450^\circ\text{C}$ where they were treated as an unknown equilibrium constant and fitted to the data. This will be discussed below.

Henry's law constants for hydrogen in water used in this study are based on the experimentally determined values at saturated water vapour pressure (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) corrected for pressure according to the semitheoretical equation of state for aqueous nonelectrolytes of Plyasunov et al. (2000) 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. All these data are consistent with one another and are in excellent agreement with the independent molecular simulation of p - V - T - X properties of binary H_2 - H_2O fluids (Suleimenov and Seward, 2002). The uncertainties in the values are considered to be $< \pm 0.05$ log units and ± 0.10 log units at 100 to 400°C and 400 to 500°C, respectively. A more thorough discussion of the calculation of Henry's law constant for hydrogen in water is given by Stefánsson and Seward (2003b).

The gold redox potential (see Eqn. 35 below) 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.

The first ionisation constant of H_2S (aq) (Eqn. 11) was taken from Suleimenov and Seward (1997) at saturated water vapour pressure, corrected for pressure using the volumes of reaction reported by Ellis and McFadden (1972) and extrapolated to 500°C using a density function. The calculation procedure is discussed in detail below.

4. RESULTS

4.1. Gold Solubility

The solubility of gold was measured in reduced aqueous sulphide solutions from 100 to 500°C at 500 bar. The results are given in Appendix B. The solubilities, measured as total dissolved gold, were in the range 3.6×10^{-8} to 6.65×10^{-4} mol kg^{-1} (0.007–131 mg kg^{-1}), in solutions of total reduced sul-

phur between 0.0164 and 0.133 mol kg^{-1} , total chloride between 0.000 and 0.240 mol kg^{-1} , total sodium between 0.000 and 0.200 mol kg^{-1} , dissolved hydrogen between 1.63×10^{-5} and 5.43×10^{-4} mol kg^{-1} and a corresponding $\text{pH}_{T,p}$ of 1.5 to 9.8. The dependence of gold solubility and solution composition was found to be complex. At neutral pH and constant sulphide and hydrogen concentrations, the solubilities were found to increase with increasing temperature. However, at pH of ~ 4 (at 25°C) and constant sulphide and hydrogen concentrations, the solubilities generally increased to a maximum plateau at $\sim 250^\circ\text{C}$, and then decreased with increasing temperature or levelled out depending on the total sulphide concentration. For acidic solution and constant sulphide and hydrogen concentrations, the solubilities were found to increase with increasing temperature. At constant pH and temperature, the solubility was found to increase with increasing sulphide concentration and decrease with increasing hydrogen concentration.

4.2. Equilibrium in Flow-Through Systems

Considerable care was taken to establish that the measured gold concentrations represented the equilibrium solubilities. Firstly, at a given temperature and fixed solution composition, a concentration plateau at variable flow rates was considered to indicate equilibrium solubility. With increasing flow rate, the gold concentrations in solution will eventually decrease below the equilibrium solubility concentration when the equilibration time is greater than the retention time of the solution in contact with the solid gold. Several experiments were carried out at fixed solution composition and temperature and variable flow rates to determine if equilibrium was reached. In Figure 2, gold solubility at 100°C for a given experiment is plotted as a function of flow rate. A concentration plateau is observed, indicating attainment of equilibrium. Several other experiments were carried out at fixed solution composition to determine if equilibrium was reached, and these too indicated that even at the maximum flow rates of the HPLC pump and low temperatures, equilibrium solubility was always attained. Secondly, the composition of the inlet solution at a given temperature and pressure was varied considerably (Appendix B) and equilibrium was thus effectively approached from different directions.

4.3. Problems With Hydrogen

Titanium is known to be very permeable to hydrogen in comparison to many other metals. The permeability of hydrogen in pure titanium has been shown to increase with increasing temperature from 8×10^{-3} to 5×10^{-2} $\text{cm}^3(\text{STP}) \text{m}^{-1} \text{s}^{-1} \text{kPa}^{-0.5}$ at 400 to 500°C, respectively (see Seward and Kishima, 1987). In addition, hydrogen is very soluble in titanium and various titanium alloys and can form hydrates on the titanium surfaces (Lewkowics, 1996). Large quantities of hydrogen can therefore diffuse into or out of the metal depending on the hydrogen potential difference and the amount of hydrogen dissolved in the titanium. Formation of a surface titanium oxide layer does not necessarily prevent these processes and cracking and discontinuities will form in the titanium oxide layer during temperature cycling of an autoclave, exposing the solutions to titanium surfaces. The hydrogen molality in the

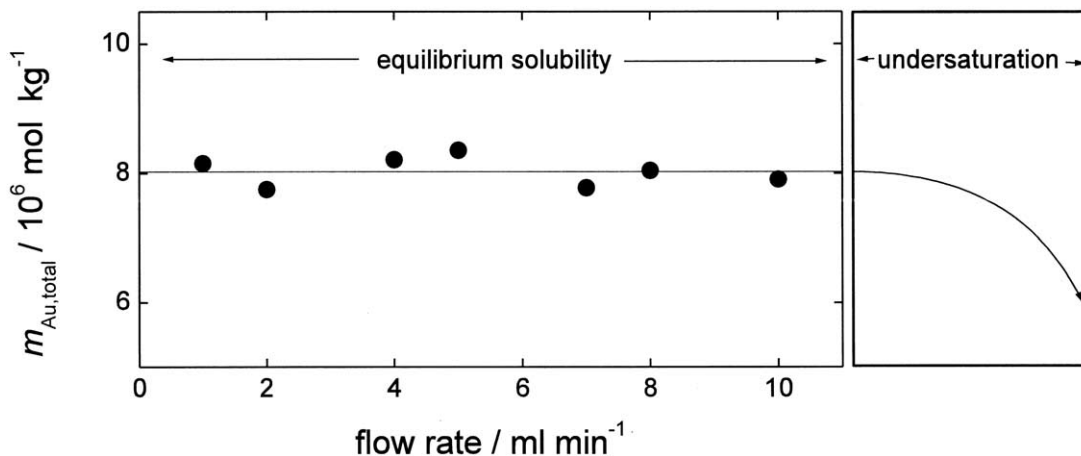


Fig. 2. The solubility of gold as a function of flow rate at 100°C, $m_{\text{S},\text{total}} = 0.0872 \text{ mol kg}^{-1}$, $m_{\text{H}_2}(\text{aq}) = 1.55 \times 10^{-4} \text{ mol kg}^{-1}$ and $m_{\text{NaOH}} = 0.0123 \text{ mol kg}^{-1}$; a concentration plateau is observed that indicates attainment of equilibrium for gold solubility. As flow rate increases, the residence time of the solution in contact with the metal becomes too short to reach equilibrium, resulting in gold undersaturation as reflected in a decrease in aqueous gold concentration.

solution can also be altered by formation of titanium hydrides and adsorption on the surface of the titanium (Lewkowics, 1996). Hydrogen loss or gain is therefore of particular concern in experiments carried out in titanium alloy autoclaves or in contact with titanium alloy surfaces.

In the beginning, our experiments were carried out using a titanium autoclave and because of possible interaction of hydrogen with the titanium considerable care and effort were taken to ensure that the hydrogen molality assumed to be reacting with the gold was the correct concentration. This is crucial for two reasons. Firstly, to determine the valence state of the dissolved gold and secondly, to be able to calculate the gold solubility constants accurately.

All the experiments in this study were carried out in a homogeneous fluid phase. Therefore, the dissolved hydrogen concentration in units of mole per kg of solvent is a fixed quantity at all temperatures and pressures as long as it is not lost or gained by secondary reactions. By measuring the dissolved hydrogen concentration in the solution (gas chromatographically) before and after it flowed through the hot autoclave, the concentration of hydrogen could be monitored and possible changes such as losses to the titanium autoclave, diffusion through the gold-lined cylinder or changes due to chemical reactions could be detected. The results are plotted in Figure 3.

The measured hydrogen molality in the inlet and outlet solution at temperatures between 100°C and 300°C using the titanium autoclave were the same within analytical uncertainties. However, at $t > 350^\circ\text{C}$ significant changes were observed. For runs containing an initial $m_{\text{H}_2}(\text{aq}) = 2$ to $3 \times 10^{-4} \text{ mol kg}^{-1}$, loss of $\sim 10\%$ was observed at 400°C whereas gains of up to 600% were observed at 440°C. For all runs containing low initial hydrogen concentrations ($< 1 \times 10^{-4} \text{ mol kg}^{-1}$) at 400 and 440°C, a considerable increase in dissolved hydrogen was observed in the outlet solution. In all cases, hydrogen was either lost to the titanium alloy pressure vessel or gained if the previous experiment had a higher hydrogen concentration. Based on these observations, it is clear that titanium is not a suitable autoclave material for solubility experiments in re-

duced hydrothermal solutions above 350°C where accurate and/or known concentrations of dissolved hydrogen are required. We therefore carried out all the equilibrium solubility experiments using a gold-lined autoclave filled with gold "sand." The permeability of hydrogen through gold is slow compared to most other metals (Seward and Kishima, 1987), thus reducing the problems of hydrogen loss and gain. As observed in Figure 3, the inlet and outlet hydrogen concentra-

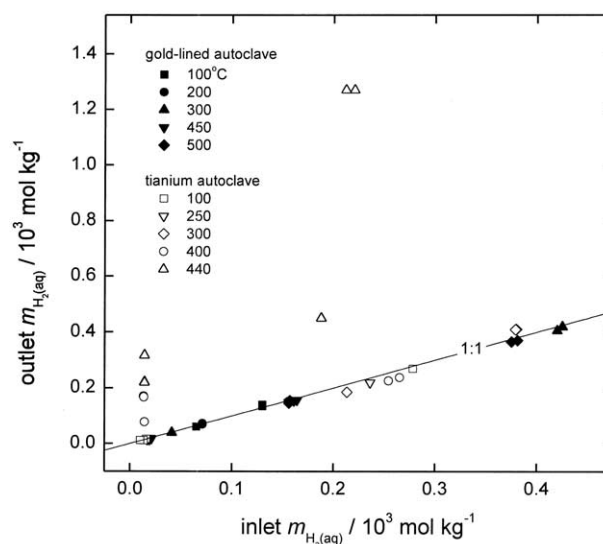
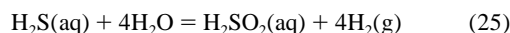
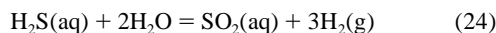
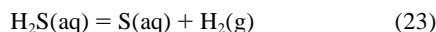


Fig. 3. Comparison of measured, dissolved hydrogen in the inlet and outlet solution as a function of temperature. The closed and open symbols represent experiments carried out with a gold-lined autoclave and titanium autoclave, respectively. An outlet to inlet ratio above or below unity indicates hydrogen gain or loss, respectively. As indicated, hydrogen was lost or gained in the experiments carried out with the titanium autoclave at $t \geq 400^\circ\text{C}$ depending on the initial hydrogen concentration and on the hydrogen concentration of the previous run(s) whereas experiments carried out with the gold-lined autoclave showed no difference in the inlet and outlet hydrogen concentration at all temperatures.

tions are practically the same at all temperatures up to 500°C in experiments carried out with the gold lined autoclave.

4.4. Disproportionation of Sulphide

Hydrogen sulphide may disproportionate in aqueous solutions to form sulphur species with higher oxidation state than -II. The reactions of main importance are



Reaction 23 is of concern at $t < 250^\circ\text{C}$ and reactions 24 and 25 at $t \geq 300^\circ\text{C}$.

Reactions involving aqueous sulphur species proceed rather slowly below 300°C (Ohmoto and Lasaga, 1982) and reliable experimental data on the kinetics of redox reactions between sulphur species at elevated temperatures in aqueous media are lacking.

Using thermodynamic data for the stability of the various sulphur species, it may be shown that the hydrogen concentrations in the experiments at $t < 450^\circ\text{C}$ are much in excess of those needed to suppress reactions 23 to 25. However, such calculations also indicate that significant SO_2 could form in the experiments at $t > 450^\circ\text{C}$. This could have been overcome by increasing the dissolved hydrogen concentrations in the experimental solutions. However, by doing this, the gold solubility would be suppressed below the detection limits of the analytical methods.

To study the disproportionation of H_2S at the highest temperatures, the total reduced sulphur was monitored before and after reacting with the gold as a function of flow rate at 450°C and 500°C. The results are plotted in Figure 4 for a solution containing $m_{\text{S}_{\text{total}}}^{-\text{II}}$ of $0.105 \text{ mol kg}^{-1}$ (the average $m_{\text{S}_{\text{total}}}^{-\text{II}}$ in the inlet solution) and $m_{\text{NaOH}} = 0.083 \text{ mol kg}^{-1}$. In addition, the total dissolved gold concentration was measured in the outlet solutions at all flow rates. As observed, the ratio of $m_{\text{S}_{\text{total}}}^{-\text{II}}$ in the inlet to that in the outlet solution was identical within analytical uncertainties ($\pm 2\%$) at all flow rates at 450°C. The same is true at 500°C for runs at flow rates $> 0.5 \text{ mL min}^{-1}$. It was only at flow rates of $\leq 0.1 \text{ mL min}^{-1}$ that $\sim 10\%$ of the initial H_2S was found to disproportionate, probably to $\text{SO}_2(\text{aq})$. All the equilibrium gold solubility experiments at $t > 400^\circ\text{C}$ were therefore carried out at flow rate of 1 mL min^{-1} . Under these conditions, at the highest temperatures, the kinetics of H_2S oxidation are thus much slower than the time required to reach equilibrium gold solubilities in the flow-through experiments. The disproportionation of H_2S was therefore considered negligible and not of concern in our flow-through experiments. However, in more conventional static solubility experiments where the experiment duration ranges from hours to days, H_2S disproportionation would be of concern at high temperatures.

5. COMPLEX FORMATION

5.1. Solubility Constants

Gold(I) prefers two-fold coordination with any type of ligand able to coordinate to soft metal cations (Schmidbaur, 1996;

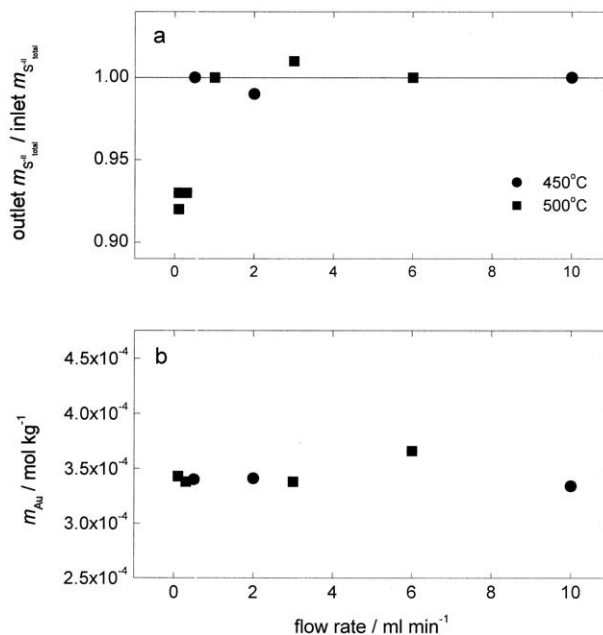
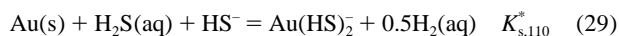
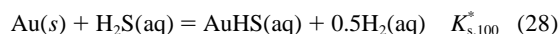


Fig. 4. Experimental determination of sulphide disproportionation and its effect on dissolved gold concentration at 450 to 500°C in experiments carried out with a gold lined stainless steel autoclave. (a) The ratio of measured total dissolved sulphide in the inlet and outlet solution as a function of flow rate at $m_{\text{S}_{\text{total}}} = 0.105 \text{ mol kg}^{-1}$ (the average concentration in the inlet solution), $m_{\text{NaOH}} = 0.083 \text{ mol kg}^{-1}$ and $m_{\text{H}_2}(\text{aq}) = 1.8$ to $2.0 \times 10^{-4} \text{ mol kg}^{-1}$. (b) The measured dissolved gold concentration in the subsequent outlet solutions. Insignificant sulphide disproportionation at flow rates $< 0.1 \text{ mL min}^{-1}$ were observed whereas no differences are observed between the inlet and the outlet solutions at and $> 0.5 \text{ mL min}^{-1}$.

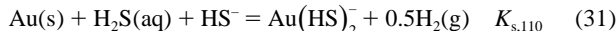
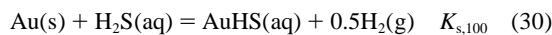
Cotton et al., 1999). In the system $\text{H}_2 + \text{H}_2\text{S} + \text{H}_2 + \text{HCl} + \text{NaOH}$, gold dissolves to produce the aqueous hydroxide and chloride gold(I) complexes, $\text{AuOH}(\text{aq})$ and AuCl_2^- (Stefánsson and Seward, 2003a, 2003b), in addition to gold(I) sulphide complexes. A number of speciation models were fitted to the data set at each temperature. These included $\text{AuOH}(\text{aq})$ and AuCl_2^- in addition to several gold(I) sulphide complexes. An example of the results and the speciation models applied at 400°C are given in Table 1. As indicated, the fit assuming $\text{AuHS}(\text{aq})$ and $\text{Au}(\text{HS})_2^-$ in addition to $\text{AuOH}(\text{aq})$ and AuCl_2^- gave the lowest overall variance, V (Eqn. 22). The contribution of the AuCl_2^- complex was never found to account for significant proportion of the measured gold concentration at any temperature and pressure. The $\text{AuOH}(\text{aq})$ complex was found to be unimportant below 400°C, whereas at 400, 450 and 500°C, $\text{AuOH}(\text{aq})$ accounted for 20, 38 and 48% of the total dissolved gold, respectively, in low pH solutions. $\text{AuOH}(\text{aq})$ accounted for $< 1\%$ in neutral solutions. Accordingly, gold dissolves in aqueous sulphide solutions according to the reactions



and in terms of hydrogen fugacity

Table 1. Non-linear least squares fitting for selected gold speciation models to the data at 400°C and 500 bar; the scheme of species (bold type) with the lowest variance, V (Eqn. 22), is considered the best fit to the experimental data; all fits include AuOH(aq) and AuCl₂.

Model	log K	V
AuHS(aq)	-5.63	55.99
HAu(HS) ₂ (aq)	-4.62	61.67
AuHS(H ₂ S) ₃ (aq)	-2.58	78.58
Au(HS) ₂ ⁻	-1.59	52.97
AuS ⁻	-2.54	52.57
H ₂ Au(HS) ₂ S ⁻	-0.18	56.49
AuHS(aq)	-5.82	1.344
Au(HS)₂⁻	-1.55	
HAu(H ₂ S) ₂ (aq)	-4.86	24.36
Au(HS) ₂ ⁻	-1.52	
AuHS(H ₂ S) ₃ (aq)	-2.78	39.35
Au(HS) ₂ ⁻	-1.52	
AuHS(aq)	-5.91	17.21
AuS ⁻	-2.59	
HAu(H ₂ S) ₂ (aq)	-6.20	22.68
AuS ⁻	-2.59	
AuHS(H ₂ S) ₃ (aq)	-4.09	36.71
AuS ⁻	-2.57	
AuHS(aq)		No convergence
H ₂ Au(HS) ₂ S ⁻		No convergence
HAu(H ₂ S) ₂ (aq)		No convergence
H ₂ Au(HS) ₂ S ⁻		No convergence
AuHS(H ₂ S) ₃ (aq)		No convergence
H ₂ Au(HS) ₂ S ⁻		No convergence



in addition to AuOH(aq), the stability of which has recently been experimentally determined in our laboratory (Stefánsson and Seward, 2003a). In sulphide solutions containing chloride, AuCl₂⁻ may be present and its activity may be calculated using the data of Stefánsson and Seward (2003b). The solubility constants, $K_{s,100}$, $K_{s,110}$, obtained by non-linear least squares treatment of all the data at a given temperature are given in Table 2 in terms of hydrogen molality and in Table 3 in terms of hydrogen fugacity and the latter equilibrium solubility constants are plotted as a function of the inverse temperature in Figures 5 and 6. The equilibrium solubility constant with respect to AuHS(aq) increases with increasing temperature from $\log K_{s,100} = -6.20 \pm 0.11$ at 200°C to -5.63 ± 0.07 to 0.11

Table 2. The experimentally derived equilibrium solubility constants, $K_{s,100}^*$ and $K_{s,110}^*$, for reactions 28 and 29, respectively, as a function of temperature at 500 bar; the uncertainties are 1σ ; the equilibrium constants are given in terms of hydrogen molality.

$t/^\circ\text{C}$	log $K_{s,100}^*$	log $K_{s,110}^*$
100	—	-3.98 ± 0.11
150	—	-3.27 ± 0.13
200	-7.72 ± 0.08	-2.86 ± 0.06
250	-7.30 ± 0.06	-2.70 ± 0.05
300	-6.96 ± 0.04	-2.65 ± 0.06
350	-6.79 ± 0.09	-2.56 ± 0.07
400	-6.77 ± 0.10	-2.50 ± 0.07
450	-6.79 ± 0.12	-2.33 ± 0.20
500	-6.73 ± 0.14	-2.20 ± 0.20

Table 3. The experimentally derived equilibrium solubility constants, $K_{s,100}$ and $K_{s,110}$, for reactions 30 and 31, respectively, as a function of temperature at 500 bar; the uncertainties are 1σ ; the equilibrium constants are given in terms of hydrogen fugacity.

$t/^\circ\text{C}$	log $K_{s,100}$	log $K_{s,110}$
100	—	-2.33 ± 0.14
150	—	-1.66 ± 0.16
200	-6.20 ± 0.11	-1.34 ± 0.08
250	-5.87 ± 0.09	-1.27 ± 0.07
300	-5.63 ± 0.07	-1.32 ± 0.09
350	-5.63 ± 0.11	-1.40 ± 0.10
400	-5.82 ± 0.12	-1.55 ± 0.10
450	-6.08 ± 0.15	-1.62 ± 0.23
500	-6.25 ± 0.19	-1.73 ± 0.25

at 300 to 350°C and then it decreases to -6.25 ± 0.19 at 500°C. The equilibrium constant for the formation of Au(HS)₂⁻ increases with temperature from $\log K_{s,110} = -2.33 \pm 0.14$ at 100°C to -1.27 ± 0.07 at 250°C but decreases subsequently to -1.73 ± 0.25 at 500°C. At $t > 450^\circ\text{C}$, AuOH(aq) contributes significantly to the total measured gold solubility and must be considered in the derivation of formation constant for the AuHS(aq). The equilibrium solubility constants for the formation of Au(HS)₂⁻ are considered most accurate at $t < 400^\circ\text{C}$. At $t > 400^\circ\text{C}$, some uncertainties arise from the extrapolation of the first ionisation constants of H₂S and the ion pair constant for NaHS(aq) which contribute significantly to the sulphide mass balance.

There are no available experimentally determined data on the dissociation constant for NaHS(aq) (Eqn. 13). Up to 400°C, they were assumed to be equivalent to those for NaCl(aq) (Ho et al., 1994). However, NaHS(aq) has little effect on the sul-

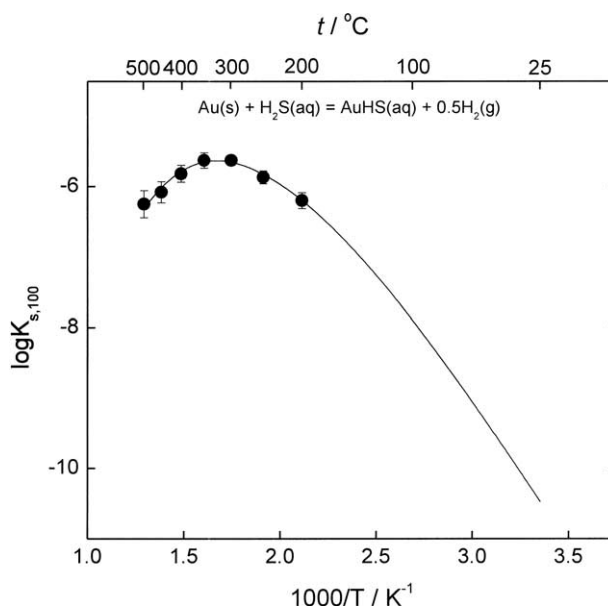


Fig. 5. The logarithm of the equilibrium solubility constant, $\log K_{s,100}$, for the species AuHS(aq), as a function of the inverse temperature at 500 bar; the symbols delineate the experimentally derived equilibrium constants (Table 3) and the line represents the fitted equation (Table 4).

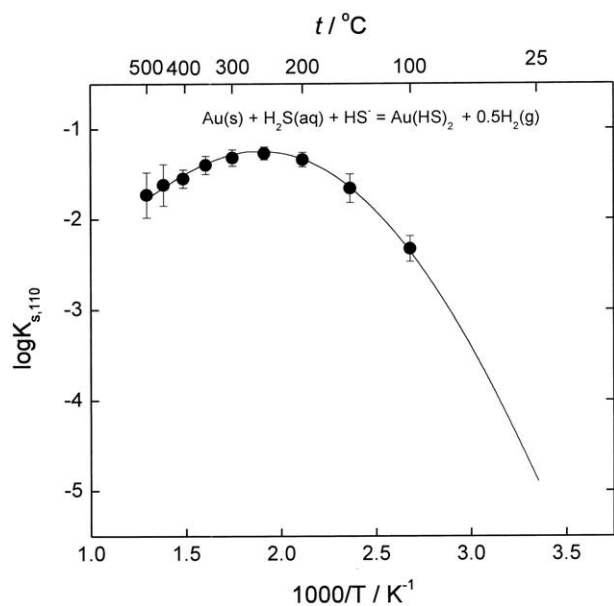


Fig. 6. The logarithm of the equilibrium solubility constant, $\log K_{s,110}$, for the species $\text{Au}(\text{HS})_2^-$, as a function of the inverse temperature at 500 bar; the symbols delineate the experimentally derived equilibrium constants (Table 3) and the line represents the fitted equation (Table 4).

phur mass balance at $t \leq 400^\circ\text{C}$. At $t > 400^\circ\text{C}$ $\text{NaHS}(\text{aq})$ is an important species and assuming $\text{NaHS}(\text{aq})$ dissociation constant to be equal to that of $\text{NaCl}(\text{aq})$, resulted in a significant positive curvature of $\log K_{s,110}$ above 400°C , suggesting that $\text{NaHS}(\text{aq})$ stability may have been overestimated. Therefore, the dissociation constant for $\text{NaHS}(\text{aq})$ was treated as an unknown equilibrium constant in the speciation calculations and fitted to the gold solubility data at $t \geq 450^\circ\text{C}$. The resulting dissociation constant according to reaction 7 was $\log K_{\text{NaHS}} = -2.51 \pm 0.05$ and -3.07 ± 0.07 at 450 and 500°C , respectively. Accordingly, $\text{NaHS}(\text{aq})$ is slightly less associated than $\text{NaCl}(\text{aq})$ at $t \geq 450^\circ\text{C}$.

The first ionisation constant of $\text{H}_2\text{S}(\text{aq})$ at 500 bar was calculated in this study from the experimentally obtained values to 350°C at saturated water vapour pressure of Suleimenov and Seward (1997), corrected for pressure using the molar volume change of reaction reported by Ellis and McFadden (1972) and extrapolated to 500°C using a density function (Gates et al., 1982; Mesmer et al., 1988) and the enthalpy and entropy of reaction (Barbero et al., 1982; Suleimenov and Seward, 1997). At $t \leq 400^\circ\text{C}$, the first ionisation constant could also be treated as an unknown variable (i.e., where K_{NaHS} was assumed to be equivalent to K_{NaCl}) and fitted to the gold solubility data. The resulting ionisation constants according to reaction 5 are compared in Figure 7 to the measured values of Suleimenov and Seward (1997) at saturated water vapour pressure and corrected for pressure and extrapolated as described above. It should be noted that the fits involving assessment of the H_2S ionisation constant from the gold solubility measurements were never used for the final evaluation of the equilibrium gold solubility constants (Tables 2 and 3). These were always based on the values given in Appendix A.

In Figure 8, the calculated solubility curves for gold in

aqueous solutions of $m_{\text{S,total}} = 0.07 \text{ mol kg}^{-1}$, $f_{\text{H}_2(\text{g})} = 10^{-2}$ bar and $a_{\text{Cl}^-} = 10^{-2.5} \text{ mol kg}^{-1}$ using the equilibrium constants given in Table 3, are compared with the measured solubilities (Appendix B) normalised to the same solution composition. As indicated, $\text{AuHS}(\text{aq})$ is the dominant complex in acidic solutions whereas $\text{Au}(\text{HS})_2^-$ predominates at neutral pH. As seen in Figures 5 and 6, the equilibrium constants for both species reach a maximum at ~ 250 to 300°C and then decrease with further increases in temperature. This is accompanied by a shift of the stability field of $\text{Au}(\text{HS})_2^-$ to more alkaline conditions in accordance with the shift of the first ionisation constant of $\text{H}_2\text{S}(\text{aq})$. As a consequence, the stability field of $\text{AuHS}(\text{aq})$ increases with increasing temperature, and at high temperature, this complex predominates at low and neutral pH's as well as under weakly alkaline conditions. The stability field of the predominant complex stoichiometry also depends on the total reduced sulphur concentration.

To generate smoothed solubility curves as a function of temperature a number of equations of the type

$$\log K = A + BT + CT^2 + D/T + E \log T \quad (32)$$

were fitted to the experimentally determined values in Table 3. The form of Eqn. 32, which best described the temperature variations of each equilibrium constant (i.e., the fewest number of parameters) was selected and the relevant coefficients are given in Table 4. The resulting calculated curves are compared with the experimental values in Figures 5 and 6.

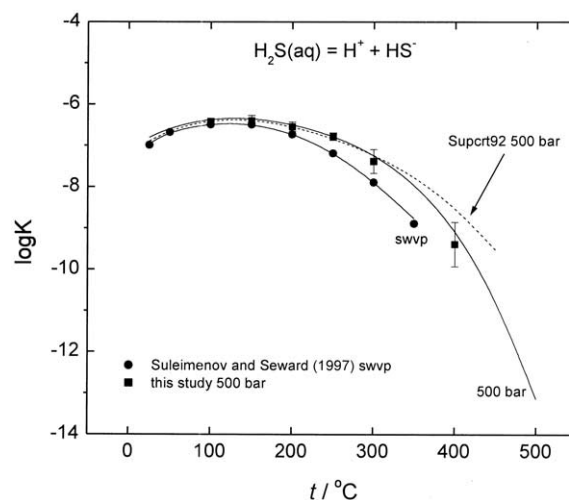


Fig. 7. The temperature and pressure dependence of the first ionisation constant of $\text{H}_2\text{S}(\text{aq})$. The solid curves are based on the experimental values of Suleimenov and Seward (1997) at saturated water vapour pressure and corrected for pressure at 500 bar according to volume of reaction given by Ellis and McFadden (1972). At $t \geq 400^\circ\text{C}$ the values for the first ionisation constant of $\text{H}_2\text{S}(\text{aq})$ were estimated using a density function (Mesmer et al., 1988) and the enthalpy and heat capacity of reaction (Barbero et al., 1982; Suleimenov and Seward, 1997). Symbols represent the experimentally derived values of Suleimenov and Seward (1997) at saturated water vapour pressure (closed circles) and values at 500 bar estimated from the gold solubility measurements of this study (closed squares). For comparison the values at 500 bar calculated using the Supcrt92 program (Johnson et al., 1992) are shown (dashed curve).

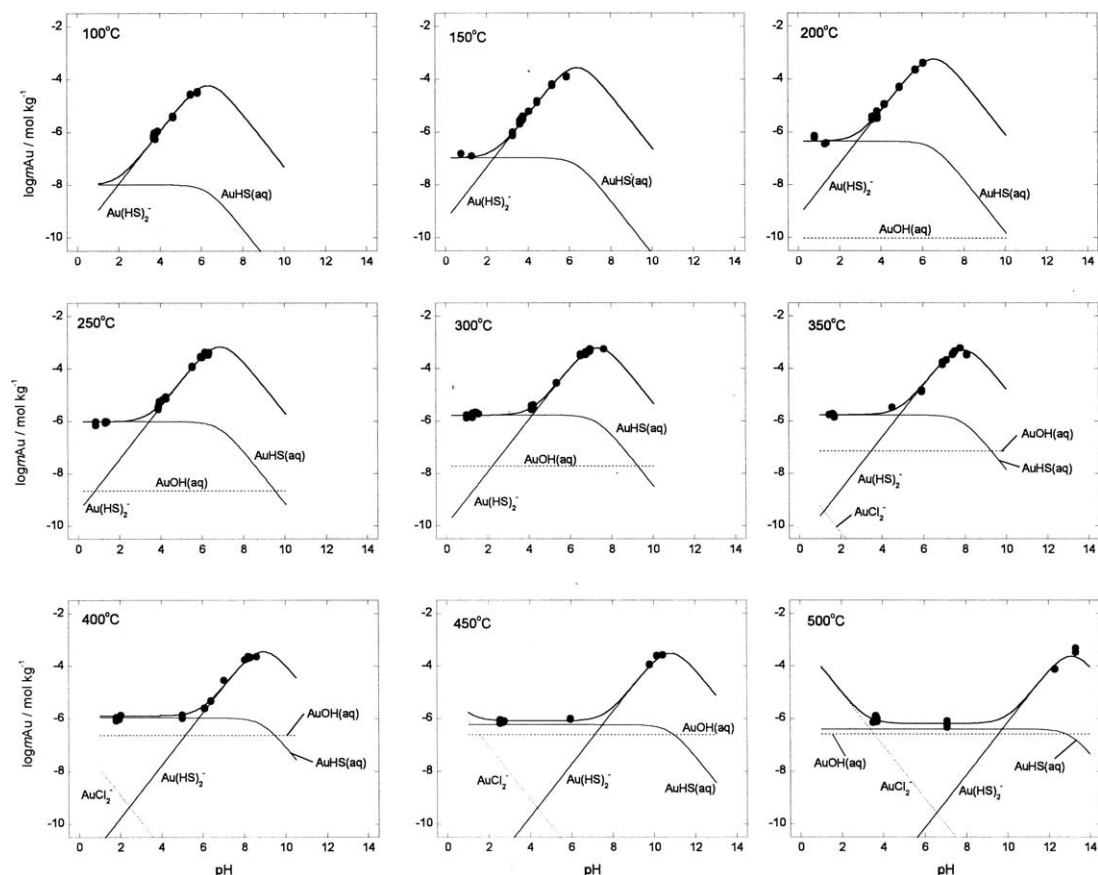
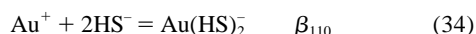
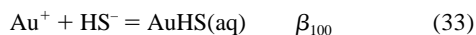


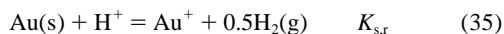
Fig. 8. The solubility of gold as a function of pH at constant $m_{S,\text{total}} = 0.07 \text{ mol kg}^{-1}$, $f_{\text{H}_2}(\text{g}) = 10^{-2} \text{ bar}$ and $a_{\text{Cl}^-} = 10^{-2.5} \text{ mol kg}^{-1}$; the curves were calculated from the equilibrium given in Table 3 and from Stefánsson and Seward (2003a, 2003b) for $\text{AuOH}(\text{aq})$ and AuCl_2^- ; the data points show the measured solubilities at the experimental pH normalised to the respective solution composition.

5.2. Cumulative and Stepwise Formation Constants

The equilibrium cumulative formation constants, β_{100} and β_{110} , for the reactions

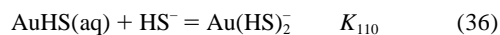


were calculated from the equilibrium constant for the gold redox reaction, $K_{s,r}$, as defined by



and the first ionisation constant of $\text{H}_2\text{S}(\text{aq})$ and the solubility constants, $K_{s,100}$ and $K_{s,110}$, determined in this study (Table 3).

From the cumulative formation constants, the stepwise formation constant



was calculated. The results are given in Table 5 and plotted in Figure 9. The formation constants were found to decrease with increasing temperature to a minimum at $\sim 400^\circ\text{C}$. Various forms of Eqn. 32 were fitted to the logarithms of the stepwise and cumulative formation constants. The results are given in Table 6 and the experimental values and the fitted curves are compared in Figure 9.

The differentiation of β_{100} and K_{110} with temperature yields the enthalpy change for the formation of $\text{AuHS}(\text{aq})$ and

Table 4. Coefficients describing the temperature variation of the gold solubility constants in terms of hydrogen fugacity (Eqn. 30 and 31) at 500 bar.

	$\log K = A + BT + CT^2 + D/T + E \log T$				
	A	B	C	D	E
$\log K_{s,100}$	12.0556	-0.012827	0	-5522.087	—
$\log K_{s,110}$	356.8770	0.050888	0	-17,204.430	-128.794

Table 5. Cumulative and stepwise formation constants as a function of temperature at 500 bar calculated from the equilibrium solubility constants derived in this study (Table 3) and literature data for $K_{s,r}$ and K_{1,H_2S} (see text); the uncertainties are 1σ .

$t/^\circ\text{C}$	$\log \beta_{100}$	$\log \beta_{110}$	$\log K_{110}$
100	—	25.55 ± 0.14	—
150	—	22.93 ± 0.16	—
200	15.96 ± 0.11	20.82 ± 0.08	4.86 ± 0.14
250	14.50 ± 0.09	19.10 ± 0.07	4.60 ± 0.11
300	13.43 ± 0.07	17.74 ± 0.09	4.31 ± 0.10
350	12.57 ± 0.11	16.80 ± 0.10	4.23 ± 0.16
400	12.12 ± 0.12	16.39 ± 0.10	4.27 ± 0.17
450	12.67 ± 0.15	17.13 ± 0.23	4.46 ± 0.32
500	13.86 ± 0.19	18.39 ± 0.25	4.53 ± 0.34

$\text{Au}(\text{HS})_2^-$ and together with Gibbs free energy of reaction, the entropy change. The values of ΔG_r^0 , ΔH_r^0 and ΔS_r^0 to 500°C at 500 bar are summarised in Table 7. The interaction of Au^+ with HS^- is a typical soft-soft, Lewis acid-base reaction where the replacement of water molecules from the hydration shell of the metal ion requires a large exothermic enthalpy. This is in line with the formation of $\text{AuHS}(\text{aq})$ which is almost entirely enthalpy driven at $t < 300^\circ\text{C}$. With increasing temperature, the formation of $\text{AuHS}(\text{aq})$ becomes endothermic with a large positive entropy indicating greater electrostatic interaction between Au^+ and HS^- . The second replacement of a water by an HS^- ligand (i.e., the stepwise formation of $\text{Au}[\text{HS}]_2^-$), shows a similar trend with increasing temperature.

6. PREVIOUS WORK

The stability of aqueous gold(I) sulphide complexes has been experimentally determined from the measured gold(I) sulphide solubility at room temperature (Belevantsev et al., 1981; Renders and Seward, 1989; Zotov et al., 1996) and from gold solubility measurements at high temperatures and pressures (Seward, 1973; Shenberger and Barnes, 1989; Hayashi and Ohmoto, 1991; Pan and Wood, 1994; Benning and Seward, 1996; Baranova and Zotov, 1998; Gibert et al., 1998; Loucks and Mavrogenes, 1999; Fleet and Knipe, 2000; Dadze et al., 2000, 2001; Baranova et al., 2002). Despite these numerous studies the results are conflicting and there are significant discrepancies amongst the various sets of data reported in the literature. The reasons for these discrepancies are thought to arise from inadequate experimental design and data interpretation of the previous studies. These include difficulties in working with hydrogen under hydrothermal conditions, sampling at high temperatures and pressures, and problems in determining the unknown gold(I) complex stoichiometries and stabilities from limited and scattered measurements in complex, multi-component solutions where many gold(I) complexes contribute to the overall gold solubility.

6.1. Gold and Gold(I) Sulphide Solubility at $\sim 25^\circ\text{C}$

Belevantsev et al. (1981) measured the solubility of gold sulphide at 20°C and 1 bar in H_2S and 3 mol/L KBr solutions with the pH adjusted by NaOH. They interpreted their results in terms of $\text{Au}(\text{HS})_2^-$, $\text{Au}_2(\text{HS})_2\text{S}_2^{2-}$ and AuHSOH^- . There are, however, several problems related to their results. In 3 mol/L

KBr solutions, the complexation of bromide with gold(I) cannot be ruled out. Furthermore, an estimation of the stability of AuHSOH^- using a theoretical approach (Dryssen et al., 1968; Byrne, 1980) and the stepwise formation constants for $\text{Au}(\text{OH})_2^-$ and $\text{Au}(\text{HS})_2^-$ (Gadet and Pouradier, 1972; Renders and Seward, 1989) indicates that the mixed AuHSOH^- complex is up to 7 orders of magnitude less stable than that reported by Belevantsev et al. (1981). In addition, attempts by Renders and Seward (1989) to prepare gold(I) sulphide by the methods given in Belevantsev et al. (1981) always resulted in large proportions of elemental gold, which would influence the solubility constant interpreted solely in terms of gold(I) sulphide solubility. It is, therefore, difficult to interpretate the results of Belevantsev et al. (1981) in terms of equilibrium gold solubility constants.

Renders and Seward (1989) measured the solubility of gold(I) sulphide at 25°C in dilute sulphide solution at pH between 2 and 12 and interpreted the results in terms of $\text{AuHS}(\text{aq})$, $\text{Au}(\text{HS})_2^-$ and $\text{Au}_2\text{S}_2^{2-}$ complex stoichiometries. Zotov et al. (1996) measured the solubility of gold(I) sulphide in near neutral pH conditions at 25°C and 1 and 500 bar. They interpreted their data in terms of $\text{Au}(\text{HS})_2^-$. The two studies are practically identical with respect to gold(I) sulphide solubility to form $\text{Au}(\text{HS})_2^-$. In both studies, great care was taken to prepare the crystalline gold(I) sulphide used in the experiments as well as oxygen-free sulphide solutions.

The equilibrium solubility constants for gold, $K_{s,100}$ and $K_{s,110}$, at 25°C and 1 bar were calculated from the gold(I) sulphide solubility constants, the solubility product of gold(I) sulphide (Baranova et al., 2002) and the gold(I) redox potential (Johnson et al., 1978). The values are listed in Table 8 and shown in Figures 10 and 11.

Recently, Baranova et al. (2002) measured the solubility of gold at 22°C and pH from 2 to 6.5 in ~ 0.1 mol/L sulphide solution and reported the results in terms of $\text{AuHS}(\text{aq})$ and $\text{Au}(\text{HS})_2^-$ (Table 8). The results are in fair agreement with the

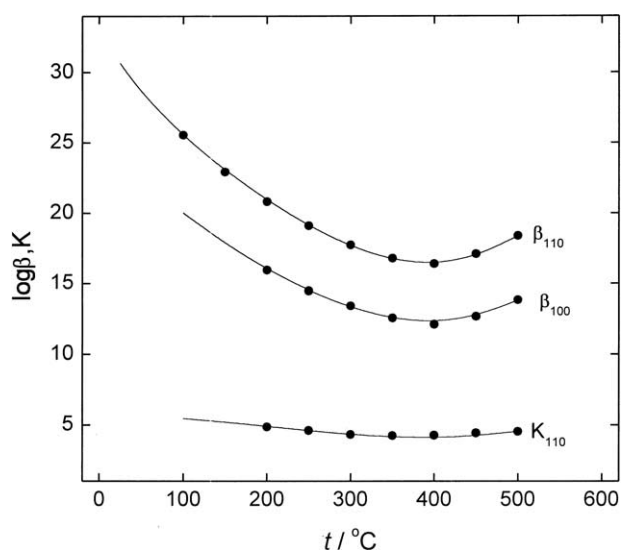


Fig. 9. The logarithm of the cumulative and stepwise formation constants of gold(I) sulphide complexes; the symbols represent the experimentally derived values (Table 5) and the line represents the fitted equation (see text).

Table 6. Coefficients describing the temperature variation of the cumulative and stepwise formation constants (Eqn. 33, 34 and 36) at 500 bar.

	$\log K = A + BT + CT^2 + D/T + E \log T$				
	A	B	C	D	E
$\log \beta_{100}$	-2594.5063	-1.0720	4.0304E-04	73,493.240	1073.715
$\log \beta_{110}$	-3043.5195	-1.3042	4.9846E-04	83,231.554	1268.789
$\log K_{110}$	-449.0131	-0.2322	9.5417E-05	9738.314	195.074

results of Renders and Seward (1989) and Zotov et al. (1996) bearing in mind the difficulties in attaining redox equilibrium in aqueous solutions at low temperatures.

6.2. Gold Solubility at High Temperatures

Seward (1973) measured gold solubility in sulphide solutions between 150 and 250°C at 1000 bar with the pH adjusted by HCl and NaOH and the hydrogen fugacity controlled by pyrite-pyrrhotite mineral buffer. He interpreted the results in terms of the three species, AuHS(aq), Au(HS)₂⁻ and Au₂(HS)₂S²⁻, which predominated in the acid, near neutral and alkaline regions of pH, respectively. The equilibrium solubility constants for the formation of Au(HS)₂⁻ determined by Seward (1973) are almost identical to those obtained in this study within experimental uncertainties (Fig. 11).

Shenberger and Barnes (1989) measured the solubility of gold between 150 and 350°C in sulphide solutions at pH from 2 to 8 and interpreted their results in terms of the Au(HS)₂⁻ complex stoichiometry. The redox state was controlled by either addition of hydrogen or the H₂S/SO₄ redox couple. The solubility constant of Shenberger and Barnes (1989) to form Au(HS)₂⁻ is much lower at $t < 250^\circ\text{C}$ compared to this study whereas the two studies agree within uncertainties at $t > 250^\circ\text{C}$. The causes for these discrepancies are unclear.

Hayashi and Ohmoto (1991) measured the solubility of gold from 250 to 350°C in sulphide solutions containing up to 4 mol/L NaCl with the hydrogen fugacity being controlled by the H₂S/SO₄ redox couple. They interpreted their results in terms of HAu(HS)₂(aq) and Au(HS)₂⁻. The H₂S/SO₄ redox couple is rarely at equilibrium at $t < 300^\circ\text{C}$ (Ohmoto and Lasaga, 1982) that in turns causes problems of controlling the hydrogen fugacity in hydrothermal solutions. Moreover, in concentrated NaCl hydrothermal solutions aqueous speciation calculations

and determination of gold solubility constants largely depends on the speciation model applied and the estimation of activity coefficients. Finally, the data of Hayashi and Ohmoto (1991) are extremely scattered and together with the overall experimental uncertainties it is difficult to assess the stoichiometry and the stability of gold(I) complexes in solution from their results.

Benning and Seward (1996) measured the solubility of gold in sulphide solutions between 150 and 400°C and 500 and 1500 bar at pH ranging from 2 to 7 and with the redox state controlled by the addition of hydrogen at room temperatures. They concluded that under these conditions AuHS(aq) and Au(HS)₂⁻ are the predominant complex stoichiometries. We have recalculated their speciation and solubility constants using the data set in Appendix A. The results are given in Table 9. The recalculated values for $K_{s,110}$ are similar to the original values reported by Benning and Seward (1996) as well as to those obtained in this study (Fig. 11). We have also recalculated the equilibrium constant, $K_{s,100}$, for AuHS(aq) from the data given by Benning and Seward (1996) and the values at various temperatures up to 300°C at 500 bar are given in Table 9 and shown in Figure 10. At 350 and 400°C, the paucity of and scatter in their data preclude an accurate evaluation of $K_{s,100}$.

Pan and Wood (1994) measured the solubility of gold, platinum and palladium from 200 to 350°C in sulphide solutions with pH between 5.9 and 9.4 and interpreted their data in terms of Au(HS)₂⁻. The resulting values are lower by up to 2 log units compared to this study (Fig. 11). The redox state was controlled by the H₂S/SO₄ buffer that is rarely at equilibrium at $t < 300^\circ\text{C}$ causing problems in calculating the hydrogen fugacity. Interaction of the metals and possible formation of solid solutions during the experiments may also have altered the measured gold solubility. Further, as observed by Pan and Wood (1994), the

Table 7. The thermodynamic properties for the stepwise formation of AuHS(aq) and Au(HS)₂⁻ at temperatures to 500°C at 500 bar, calculated from the coefficients given in Table 6.

$t/^\circ\text{C}$	$\Delta G_f^0/\text{kJ mol}^{-1}$		$\Delta H_f^0/\text{kJ mol}^{-1}$		$\Delta S_f^0/\text{J mol}^{-1} \text{K}^{-1}$	
	AuHS(aq)	Au(HS) ₂ ⁻	AuHS(aq)	Au(HS) ₂ ⁻	AuHS(aq)	Au(HS) ₂ ⁻
100	-143.0	-38.9	-131.6	-10.3	31	77
150	-144.5	-42.2	-134.9	-19.2	22	54
200	-145.1	-44.4	-142.9	-27.1	5	37
250	-145.2	-46.0	-144.0	-31.3	2	28
300	-145.9	-47.4	-126.6	-29.1	34	32
350	-149.3	-49.4	-79.1	-17.7	113	51
400	-158.1	-52.8	10.0	5.7	250	87
450	-175.4	-58.4	152.3	43.7	453	141
500	-204.7	-67.2	359.4	99.1	730	215

Table 8. The equilibrium solubility constants, $K_{s,100}$ and $K_{s,110}$, at room temperature.

$t/^\circ\text{C}$	p/bar	R89 ^{ab}	Z96 ^{ab}	B02 ^{ac}
$\log K_{s,100}$				
25	1	-10.54		
22	1			-11.16
$\log K_{s,110}$				
25	1	-4.94	-4.96	
25	500		-5.1	
22	1			-5.65

^a R89: Renders and Seward (1989); Z96: Zotov et al. (1996); B02: Baranova et al. (2002).

^b Calculated from gold(I) sulphide solubility measurements.

^c Measured gold(I) solubility.

use of a titanium frit at the internal end of the sampling tube may have caused a local increase in hydrogen concentration that may in turn have suppressed the measured gold concentrations and the calculated equilibrium solubility constant.

Gibert et al. (1998) measured the solubility of gold in 0.5 *m* KCl solutions at temperatures from 350 to 450°C and pressures of 500 bar. The activity of H₂S and hydrogen fugacity were controlled by either pyrite-pyrrhotite-magnetite or pyrite-magnetite-hematite mineral assemblages and the pH was controlled by the quartz-Kfeldspar-muscovite mineral buffer. Gibert et al. (1998) interpreted their results in terms of AuHS(aq). The use of mineral buffers and a supporting salt (KCl) for controlling the solution composition gives rise to difficulties in interpreting the gold solubility data. All components (Fe, K, Cl, H, O, Au, S, Al and Si) and independent equilibrium reactions have to be included in the aqueous speciation and the calculation of the gold(I) solubility constants and the results dependent upon

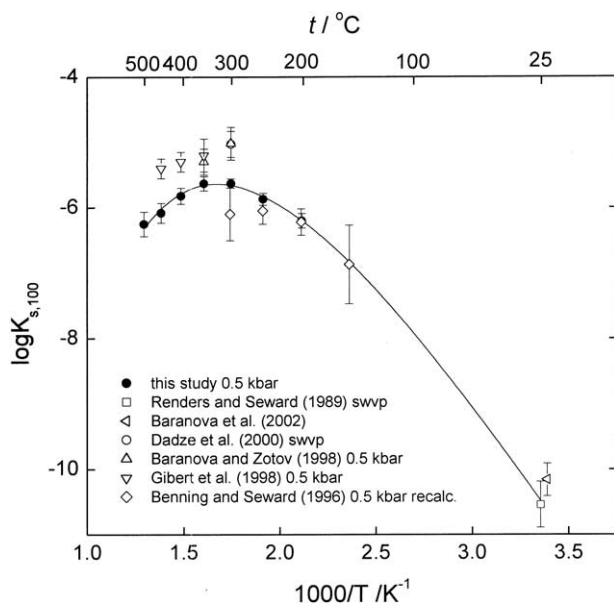


Fig. 10. The logarithm of the equilibrium solubility constant, $\log K_{s,100}$, for the species AuHS(aq), as a function of the inverse temperature derived in this study and compared with literature values; the line represents the fitted equation (Table 4) of this study.

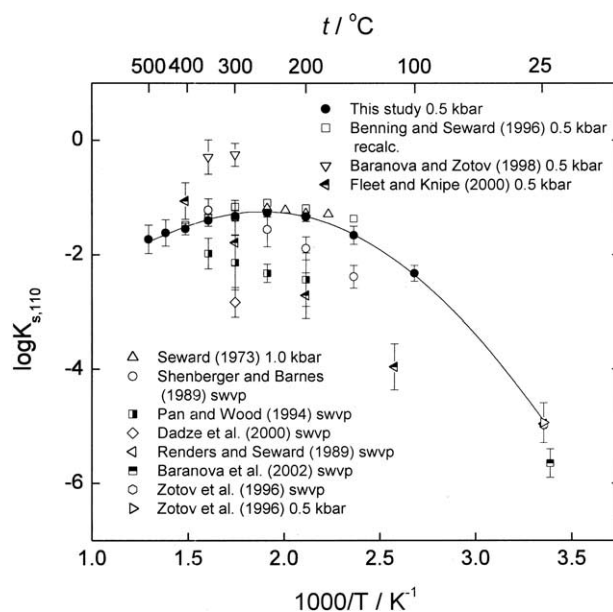


Fig. 11. The logarithm of the equilibrium solubility constant, $\log K_{s,110}$, for the species Au(HS)₂⁻ as a function of the inverse temperature derived in this study and compared with literature values; the line represents the fitted equation (Table 4) of this study.

literature values. Gibert et al. (1998) used different sources for the equilibrium constants compared to this study. Therefore, to compare the measured solubilities of the two studies, the aqueous speciation based on the results of Gibert et al. (1998) was recalculated using the thermodynamic database consistent with the present study. Gibert et al. (1998) reported a much higher gold solubility constant to form AuHS(aq) ($K_{s,100}$) compared to this study (Fig. 11). As seen in Figure 12 this is caused by incorrect data interpretation assuming only AuHS(aq) to be present whereas the solubilities are caused by three gold(I) complexes, AuOH(aq), AuHS(aq) and Au(HS)₂⁻.

Loucks and Mavrogenes (1999) measured the solubility of gold in up to 1 *m* total Cl solution at temperatures from 550 to 725°C and pressures from 1 to 4 kbar. The activity of H₂S and hydrogen fugacity and pH were controlled by pyrite-pyrrhotite-magnetite and quartz-K-feldspar-muscovite mineral buffers, respectively. They interpreted their results in terms of an AuHS(H₂S)₃(aq) complex. This gold(I) sulphide complex stoichiometry is inconsistent with theoretical studies and structural

Table 9. The logarithm of the equilibrium solubility constants, $\log K_{s,100}$ and $\log K_{s,110}$, for reactions 30 and 31 at 500 bar calculated from the experimental results of Benning and Seward (1996) using the same approach as in this study and the data base in Appendix A; the uncertainties are 1σ .

$t/^\circ\text{C}$	$\log K_{s,100}$	$\log K_{s,110}$
150	-6.87 ± 0.60	-1.37 ± 0.10
200	-6.22 ± 0.20	-1.19 ± 0.10
250	-6.05 ± 0.20	-1.09 ± 0.10
300	-6.10 ± 0.40	-1.16 ± 0.10
350	—	-1.35 ± 0.14
400	—	-1.48 ± 0.05

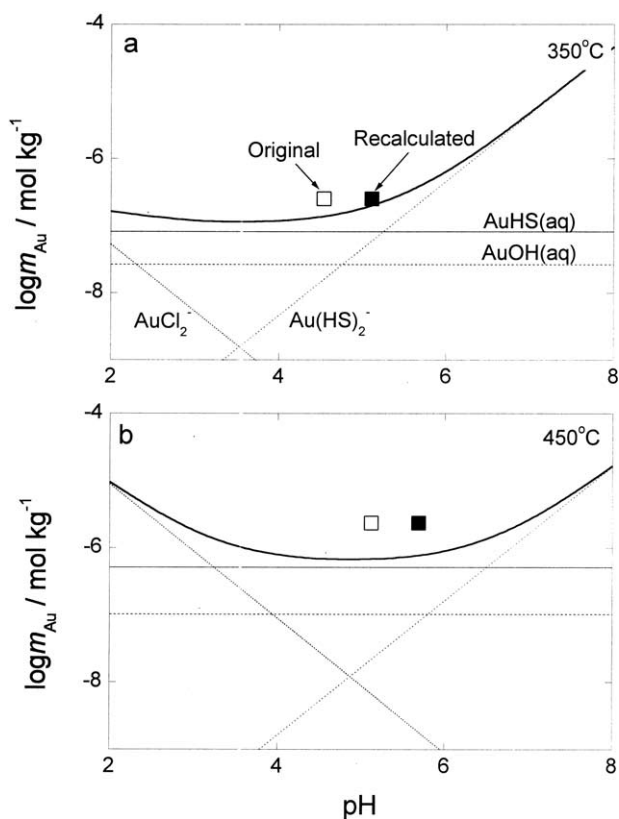


Fig. 12. A comparison of the measured gold solubilities of Gibert et al. (1998) with the calculated gold solubilities due to AuOH(aq) and AuCl_2^- determined by Stefánsson and Seward (2003a, 2003b) and AuHS(aq) and Au(HS)_2^- determined in this study (Table 3); open square represent the original pH given by Gibert et al. (1998) and the solid square the recalculated pH value (see text). As seen, the calculated pH values are highly dependent on the thermodynamic data base used for the speciation calculations and that three species contribute to the overall solubility, AuOH(aq) , AuHS(aq) and Au(HS)_2^- , but not only AuHS(aq) as argued by Gibert et al. (1998)

determination of inorganic gold(I) complexes (Nemukhin et al., 1998; Schmidbaur, 1996; Tossel, 1996; Cotton et al., 1999). Instead, gold(I), with its $5d^{10}$ electronic configuration, prefers twofold coordination normally with “soft” (Lewis base) electron donors. Therefore, we have re-evaluated the data of Loucks and Mavrogenes (1999) assuming that the AuOH(aq) , AuCl_2^- , AuHS(aq) and Au(HS)_2^- species account for their measured solubilities. The results indicate that their solubilities are most likely caused by two or more gold(I) species, AuCl_2^- in acidic 1 M chloride solutions and Au(HS)_2^- neutral chloride free solutions, respectively, as well as by AuHS(aq) and possibly AuOH(aq) . An example is shown in Figure 13 assuming AuHS(aq) , AuCl_2^- and Au(HS)_2^- gold(I) complexes to be present. However, the exact gold(I) complex stoichiometries and stabilities cannot be determined from the experimental results of Loucks and Mavrogenes (1999) because of limited number of data points, the limited concentration ratio of many of the key parameters (H_2S , H_2 and pH), the very high uncertainties ($\pm 30\%$ and more) in the analytical data for the measured solubilities as well as the actual data scatter. In fact, the outcome is a circular argument depending on the gold(I) spe-

ciation model used and thermodynamic database applied for the aqueous speciation calculations.

Baranova and Zotov (1998) measured the solubility of gold in sulphide solutions from 300 to 350°C at 500 bar with the solution pH ranging from 1.5 to 6. Metallic aluminium was used as a source of hydrogen and H_2S was generated from the decomposition of thioacetamide (CH_3CSNH_2). They interpreted their results in terms of AuHS(aq) and Au(HS)_2^- . Dadze et al. (2000, 2001) measured the gold solubility at 300°C and pH of 7.4 in a similar way to Baranova and Zotov (1998) except that the redox state was controlled by the $\text{H}_2\text{S}/\text{SO}_4$ couple. Both these studies obtained very different solubility constants compared to this study for both complexes (Figs. 10 and 11). These discrepancies are considered to be caused by experimental difficulties. Firstly, Baranova and Zotov (1998) and Dadze et al. (2000, 2001) carried out their experiments in a titanium autoclave and interaction of dissolved hydrogen with titanium is of particular concern at high temperatures as we have previously discussed. Secondly, under hydrothermal conditions, thioacetamide will disproportionate to form CO_2 , N_2 , H_2S , CH_4 , H_2 and NH_3 , and subsequently H_2S may be oxidised to SO_4 or sulphur species of intermediate oxidation state and this has been confirmed by Raman spectroscopy (Dadze et al., 2000, 2001). Therefore, the solution composition and hydrogen fugacity in these experiments is not well constrained and accurate assessment of gold(I) solubility constants are difficult.

Fleet and Knipe (2000) measured the solubility of gold from 100 to 400°C and 1500 bar in 20.6 mol kg^{-1} sulphide solutions. This high H_2S concentration is sufficient to stabilise S^0 , and the reaction between H_2S and S^0 was assumed to control the redox state of the solutions. Fleet and Knipe

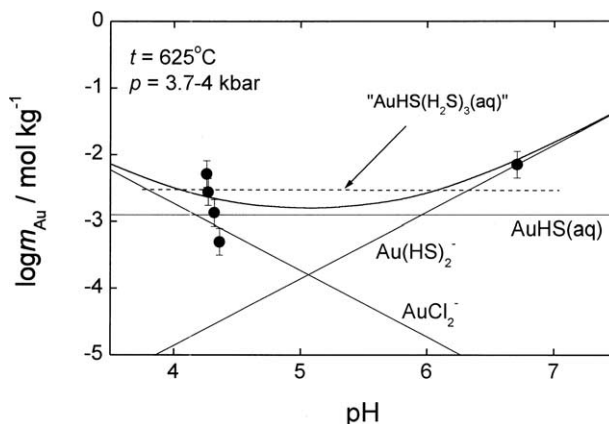


Fig. 13. A comparison of the measured gold solubilities of Loucks and Mavrogenes (1999) with a possible gold(I) speciation model as a function of pH at constant $a_{\text{H}_2\text{S(aq)}} = 1.0 \text{ mol kg}^{-1}$, $f_{\text{H}_2(\text{g})} = 0.5 \text{ bar}$ and $a_{\text{Cl}^-} = 0.3 \text{ mol kg}^{-1}$; the symbols represent the experimental results of Loucks and Mavrogenes (1999) at the respective solution composition, the thin solid lines represent the solubility due to variable gold(I) complexes and the solid curve the total solubility. The dashed line represent the fit of Loucks and Mavrogenes (1999) forming a $\text{AuHS(H}_2\text{S)}_3\text{(aq)}$ complex, a gold(I) complex stoichiometry that is inconsistent with theoretical studies and structural determination of inorganic gold(I) complexes (Nemukhin et al., 1998; Schmidbaur, 1996; Tossel, 1996; Cotton et al., 1999).

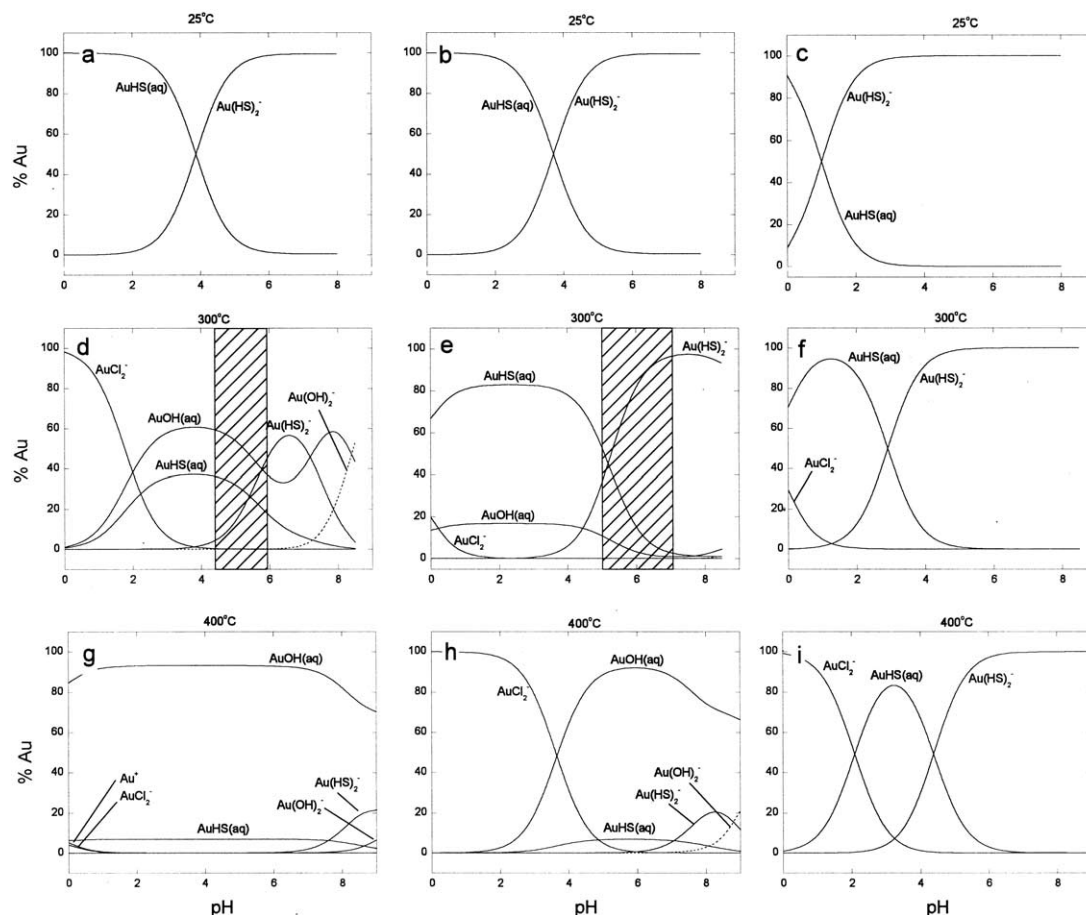


Fig. 14. The percentage distribution of gold(I) species as a function of solution composition and temperature at 500 bar: (a) and (g) $m_{\text{S}^{\text{II}}} = 0.001$ and $m_{\text{Cl}^-} = 0.001$; (b) and (h) $m_{\text{S}^{\text{II}}} = 0.001$ and $m_{\text{Cl}^-} = 0.5$; (d) high-temperature geothermal seawater at Reykjanes, Iceland with total $m_{\text{S}^{\text{II}}} = 5.0 \times 10^{-4}$ and $m_{\text{Cl}^-, \text{total}} = 0.61$ (Arnórsson et al., 1983); (e) dilute natural high-temperature geothermal water at Ohaaki-Broadlands with total $m_{\text{S}^{\text{II}}} = 0.004$ and $m_{\text{Cl}^-, \text{total}} = 0.03$ (Mahon and Finlayson, 1972; DSIR files); (c), (f) and (i) $m_{\text{S}^{\text{II}}} = 0.50$ and $m_{\text{Cl}^-} = 0.50$; the shaded areas represent typical pH values found for the respective water type at aquifer temperature; the complex stabilities used for these calculations are based on experimental data of this study and Stefánsson and Seward (2003a, 2003b); the dashed line represent maximum stability of $\text{Au}(\text{OH})_2^-$.

(2000) interpreted their results in terms of $\text{Au}(\text{HS})_2^-$. Their resulting solubility constant $K_{\text{s},110}$ is lower by up to 2 log units compared to this study (Fig. 11). This discrepancy can be related to experimental problems and data interpretation. Firstly, Fleet and Knipe (2000) carried out the experiments in gold capsules. Upon quenching, most of the dissolved gold probably precipitated as gold(I) sulphide and/or elemental gold and this resulted in very large uncertainties in estimating the dissolved gold at experimental temperatures. Secondly, the aqueous speciation calculations in 20.6 mol kg^{-1} sulphide solutions are largely dependent on the speciation/activity model and thermodynamic data base used and has to be viewed as an approximation. Thirdly, the redox kinetics involving sulphur species are slow below 300°C and overall redox equilibrium between the H_2S and S^0 may not have been reached in the experiments (Ellis and Giggenbach, 1971; Ohmoto and Lasaga, 1982). It is therefore clear that the experiments of Fleet and Knipe (2000) do not permit an accurate determination of the thermodynamic stability of dissolved gold(I) complexes.

7. AQUEOUS SPECIATION AND TRANSPORT OF GOLD BY HYDROTHERMAL FLUIDS

7.1. Speciation of Gold in Aqueous Solutions

The percentage distribution of gold(I) complexes in solution as a function of solution composition and temperature is shown in Figure 14. The solution compositions used for these calculations are those typically found in natural environments for solutions containing a range of sulphide and chloride concentrations. At 100°C and m_{Cl^-} to 0.5 mol kg^{-1} , gold(I) sulphide complexes predominate at all pH's (Figs. 14a–14c). At 300°C the same is true (Figs. 14d–14f) except at very low sulphide concentrations and in chloride rich solutions where $\text{AuOH}(\text{aq})$ and AuCl_2^- become important (Fig. 14d). However, at 400°C, the predominant gold(I) complexes are insensitive to the solution composition (Figs. 14h and 14i). In dilute sulphide and chloride solutions, $\text{AuOH}(\text{aq})$ predominates at all pH values (Fig. 14h), whereas in dilute sulphide and 0.5 mol kg^{-1} Cl solution, AuCl_2^- is the most important species below pH of ~ 4 and $\text{AuOH}(\text{aq})$ predominates in neutral and alkaline solutions

(Fig. 14h). In concentrated sulphide and chloride solutions AuCl_2^- , $\text{AuHS}(\text{aq})$ and $\text{Au}(\text{HS})_2^-$ become the predominant species with increasing pH (Fig. 14i).

7.2. Transport of Gold by Hydrothermal Fluids

Hydrothermal gold ore deposits are formed as a consequence of instability of gold complexes transported by fluids in the Earth's crust. Changes in temperature, pressure, ligand activity, phase separation, boiling, mixing and sulphide mineral precipitation can lead to gold deposition.

Insight into the processes influencing gold transport and deposition can be obtained by studying the geochemistry of gold in geothermal systems. Active geothermal systems such as at Ohaaki-Broadlands and Rotokawa, New Zealand (Brown, 1986; Krupp and Seward, 1987; Weissberg et al., 1979), the geothermal seawater system at Reykjanes, Iceland (Hardar-dóttir et al., 2001), the Salton Sea, California (e.g., McKibben et al., 1988) and Cerro Prieto, Mexico (Clark and Williams-Jones, 1990) can transport and deposit significant quantities of gold. For example, silicate and sulphide scales are common in pipelines at Reykjanes, and may contain up to 93 ppm gold (Hardar-dóttir et al., 2001). At Rotokawa, sulphide-rich surface muds contain up to 50 ppm gold (Krupp and Seward, 1987) and are still being deposited at present.

The fluid chemistry at Ohaaki-Broadlands has been extensively studied (e.g., Mahon and Finlayson, 1972) and analytical data on gold concentrations in the aquifer are available for a number of wells (Brown, 1986; Brown and Webster, 1998). The fluid chemistry with respect to major components at Reykjanes is also well known (e.g., Arnórsson et al., 1983) but no data are currently available on the gold concentration of the aquifer fluids at Reykjanes. For the Ohaaki-Broadlands system, the aquifer fluid composition and speciation were calculated from analytical data given by Mahon and Finlayson (1972) and New Zealand DSIR file reports as well as by Brown (1986) and Brown and Webster (1998) with the aid of the WATCH computer program (Arnórsson et al., 1982; Bjarnason, 1994). In the present study, a supplement was added to the program to include data on gold(I) sulphide, chloride and hydroxide complexes obtained in this study and by Stefánsson and Seward

(2003a, 2003b). The measured and calculated gold concentration in the aquifer fluid and the distribution of gold species at Ohaaki-Broadlands are given in Table 10. For comparison, the estimated equilibrium gold concentration and species distribution for the saline geothermal fluids at Reykjanes is also listed in Table 10. As indicated, the measured gold concentrations in the Ohaaki-Broadlands fluids are >1 order of magnitude less than the theoretical values assuming equilibrium with native gold. However, it is clear that overall redox equilibrium has not been reached in many geothermal systems and gold availability in the primary rocks may be limited. Ancillary processes may also control the dissolved gold content of the Ohaaki-Broadlands fluids such as the substitution of gold into minerals like electrum or adsorption of gold by other phases like pyrite (Widler and Seward, 2002).

The effects of conductive cooling and closed system adiabatic boiling on the transport of gold in the Ohaaki-Broadlands fluids and for the geothermal seawater at Reykjanes are shown in Figure 15. The calculations were performed using the WATCH program (Arnórsson et al., 1982; Bjarnason, 1994). Gold was found to be mobile upon initial adiabatic boiling whereas extensive boiling leads to quantitative gold loss. However, as demonstrated by Seward (1989), open system boiling leads to quantitative loss of gold upon <10% boiling for the dilute fluids at Ohaaki-Broadlands. Phase separation in active geothermal systems is generally intermediate between adiabatic and open system boiling. For both geothermal systems, cooling of the fluids leads to a decrease in gold solubility but not focussed deposition.

8. CONCLUSIONS

The solubility of gold was measured in sulphide solutions between 100 and 500°C at 500 bar. The solubilities were in the range from 3.6×10^{-8} to 6.65×10^{-4} mol kg^{-1} (0.007–131 mg kg^{-1}) in solutions of total sulphide between 0.0164 and 0.133 mol kg^{-1} , total chloride between 0.000 and 0.240 mol kg^{-1} , total sodium between 0.000 and 0.200 mol kg^{-1} , total dissolved hydrogen between 1.63×10^{-5} and 5.439×10^{-4} mol kg^{-1} and with a corresponding $\text{pH}_{T,p}$ varying from 1.5 to 9.8. A non-linear least squares treatment of the data demon-

Table 10. Measured and calculated gold concentration of the aquifer fluid and aqueous gold speciation at Ohaaki-Broadlands (BR), New Zealand, and Reykjanes (REK), Iceland.

	BR 22, Well 22	BR 9, Well 9	BR 20, Well 20	REK 8, Well 8
$t/^\circ\text{C}$	271 ^a	289 ^a	298 ^a	244 ^b
Measured $m_{\text{Au,total}}/\text{ppb}$	1.5 ^c	0.86–1.03 ^d	0.50–1.16 ^d	n.a.
Calculated $m_{\text{Au,total}}/\text{ppb}^e$	42	23	33	2
<i>Speciation</i>				
Au^+	<0.1%	<0.1%	<0.1%	<0.1%
$\text{AuOH}(\text{aq})$	1%	4%	5%	15%
$\text{Au}(\text{OH})_2^-$	<0.1%	<0.1%	<0.1%	<0.1%
AuCl_2^-	<0.1%	<0.1%	<0.1%	<0.1%
$\text{AuHS}(\text{aq})$	15%	29%	34%	58%
$\text{Au}(\text{HS})_2^-$	84%	67%	61%	27%

^a Reservoir temperature estimated using the quartz geothermometer (Fournier and Potter, 1982).

^b Measured aquifer temperature.

^c Minimum number taken from Brown (1986).

^d Concentration in deep geothermal fluids taken from Brown and Webster (1998).

^e Calculated total dissolved gold in equilibrium with elemental gold.

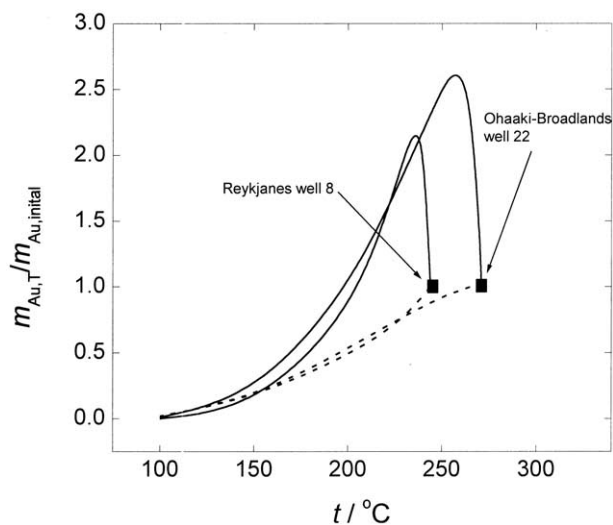


Fig. 15. The effect of conductive cooling (broken lines) and adiabatic boiling (solid lines) on gold concentration assuming that dissolved gold in solution is determined by native gold solubility; $m_{\text{Au},T}/m_{\text{Au,initial}}$ is the ratio between the equilibrium gold solubility at a given temperature T and the initial equilibrium solubility at the aquifer fluid temperature.

strated that the solubility of gold in aqueous sulphide solutions of acidic to neutral pH can be accurately described by the formation of $\text{AuHS}(\text{aq})$ and $\text{Au}(\text{HS})_2^-$. In addition, $\text{AuOH}(\text{aq})$ is an important complex in dilute acidic solutions at $t > 400^\circ\text{C}$. The solubility constant to form $\text{AuHS}(\text{aq})$ was found to increase from $\log K_{s,100} = -6.20 \pm 0.11$ at 200°C to a maximum of -5.63 ± 0.07 to 0.11 at 300 to 350°C and then decrease to -6.25 ± 0.19 at 500°C . The solubility constant to form $\text{Au}(\text{HS})_2^-$ increases with increasing temperature from $\log K_{s,110} = -2.33 \pm 0.14$ at 100°C to -1.27 ± 0.07 at 250°C and then decreases to -1.73 ± 0.25 at 500°C . Based on these data and the solubility product of gold, the stepwise and cumulative formation constants were also calculated. The dominant gold(I) species in solution are dependent on temperature and fluid composition. At low temperatures, gold(I) sulphide complexes predominate whereas at higher temperatures, gold(I) hydroxide and chloride complexes become increasingly more important in dilute and concentrated acidic chloride solutions, respectively. Excessive boiling of both dilute and saline geothermal water leads to quantitative loss of gold from solution. On the other hand, conductive cooling may lead to a decrease of dissolved gold in hydrothermal solutions but not to focussed deposition as required for ore formation.

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APPENDIX A

Logarithms of the equilibrium constants at 500 bar used for the speciation calculations.

Reaction	t/°C										Source
	100	150	200	250	300	350	400	450	500		
H ₂ S(aq) = H ⁺ + HS ⁻	-6.32	-6.36	-6.55	-6.88	-7.32	-7.92	-8.92 ^f	-10.8 ^f	-13.1 ^f		b
H ₂ O(l) = H ⁺ + OH ⁻	-12.10	-11.45	-11.05	-10.85	-10.87	-11.14	-11.88	-13.74	-16.13		c
HCl(aq) = H ⁺ + Cl ⁻	0.62	0.41	0.14	-0.41	-0.98	-1.64	-2.54	-4.13	-6.03		d
NaOH(aq) = Na ⁺ + OH ⁻	0.07	-0.26	-0.56	-0.85	-1.17	-1.54	-2.05	-2.94	-3.63		e
NaHS(aq) = Na ⁺ + HS ⁻	0.72	0.42	0.15	-0.16	-0.51	-0.95	-1.59	-2.51 ^f	-3.08 ^f		g
H ₂ (g) = H ₂ (aq)	-3.30	-3.22	-3.04	-2.86	-2.66	-2.32	-1.90	-1.42	-0.95		f
Au(s) + H ⁺ = Au ⁺ + 0.5 H ₂ (g)	-21.56	-18.23	-15.61	-13.49	-11.74	-10.28	-9.02	-7.95	-7.01		a

^a Supert92, Johnson et al. (1992).

^b Suleimenov and Seward (1997) corrected for pressure using ΔV_r from Ellis and McFadden (1972).

^c Marshall and Franck (1981).

^d Ho et al. (2001) extrapolated at $t > 400^\circ\text{C}$.

^e Ho and Palmer (1996).

^f See text.

^g Taken to be equivalent to NaCl(aq) = Na⁺ + Cl⁻ as measured by Ho et al. (1994).

APPENDIX B

Experimental results at p = 500 bar.

$m_{\text{S,total}}/\text{mol kg}^{-1}$	$m_{\text{NaOH}}/\text{mol kg}^{-1}$	$m_{\text{HCl}}/\text{mol kg}^{-1}$	$m_{\text{H}_2(\text{aq})}/\text{mol kg}^{-1}$	$m_{\text{Au,total}}/\text{mol kg}^{-1}$
t = 100°C				
8.000E-02			1.57E-04	1.87E-07
8.000E-02			1.57E-04	2.22E-07
7.400E-02			3.97E-04	4.76E-06
7.400E-02			3.96E-04	4.16E-06
8.661E-02			1.66E-04	1.94E-07
8.661E-02			1.66E-04	1.58E-07
8.661E-02			1.66E-04	2.03E-07
6.240E-02			3.18E-04	5.4E-08
6.240E-02			3.18E-04	8.3E-08
9.083E-02	2.000E-04		1.75E-04	3.14E-07
7.620E-02	1.510E-03		1.51E-04	8.11E-07
7.620E-02	1.510E-03		1.51E-04	9.26E-07
8.720E-02	1.231E-02		1.55E-04	7.80E-06
8.720E-02	1.231E-02		1.55E-04	8.39E-06
t = 150°C				
8.000E-02			1.58E-04	7.41E-07
8.000E-02			1.57E-04	8.39E-07
7.400E-02	2.000E-02		4.00E-04	1.94E-05
7.400E-02	2.000E-02		3.95E-04	1.75E-05
7.100E-02		6.800E-02	7.86E-05	3.6E-08
7.100E-02		6.800E-02	7.86E-05	3.6E-08

APPENDIX B. (Continued)

$m_{S,\text{total}}/\text{mol kg}^{-1}$	$m_{\text{NaOH}}/\text{mol kg}^{-1}$	$m_{\text{HCl}}/\text{mol kg}^{-1}$	$m_{\text{H}_2(\text{aq})}/\text{mol kg}^{-1}$	$m_{\text{Au},\text{total}}/\text{mol kg}^{-1}$
8.800E-02		2.400E-01	7.86E-05	5.3E-08
7.760E-02			1.99E-04	6.51E-07
7.760E-02			2.00E-04	8.52E-07
7.760E-02			1.99E-04	7.74E-07
8.060E-02			2.07E-04	6.51E-07
8.060E-02			2.07E-04	7.05E-07
7.170E-02			1.84E-04	6.78E-07
7.170E-02			1.84E-04	6.14E-07
7.170E-02			1.84E-04	7.28E-07
9.390E-02			2.44E-04	9.18E-07
9.390E-02			2.42E-04	8.60E-07
9.390E-02			2.44E-04	7.51E-07
9.190E-02			2.37E-04	8.17E-07
9.190E-02			2.38E-04	8.21E-07
9.190E-02			2.37E-04	8.63E-07
9.040E-02			2.33E-04	8.99E-07
9.040E-02			2.33E-04	7.98E-07
8.137E-02		1.000E-04	2.10E-04	6.60E-07
8.137E-02		1.000E-04	2.09E-04	4.91E-07
8.137E-02		1.000E-04	2.09E-04	5.07E-07
8.100E-02		5.000E-04	2.07E-04	2.43E-07
8.100E-02		5.000E-04	2.07E-04	2.13E-07
8.100E-02		5.000E-04	2.07E-04	1.76E-07
5.921E-02	2.000E-04		7.88E-05	1.30E-06
5.921E-02	2.000E-04		7.88E-05	1.30E-06
5.917E-02	7.000E-04		8.35E-05	3.22E-06
5.917E-02	7.000E-04		8.30E-05	3.05E-06
5.917E-02	7.000E-04		8.24E-05	2.80E-06
5.841E-02	3.940E-03		1.04E-04	1.20E-05
5.841E-02	3.940E-03		1.08E-04	1.35E-05
5.841E-02	3.940E-03		1.04E-04	1.18E-05
$t = 200^\circ\text{C}$				
8.000E-02			1.57E-04	1.01E-06
8.000E-02			1.58E-04	1.14E-06
7.400E-02	2.000E-02		4.00E-04	7.18E-05
7.400E-02	2.000E-02		3.99E-04	7.67E-05
7.100E-02		6.800E-02	7.86E-05	1.22E-07
7.100E-02		6.800E-02	7.86E-05	1.22E-07
8.800E-02		2.400E-01	7.87E-05	2.54E-07
8.800E-02		2.400E-01	7.87E-05	3.05E-07
9.340E-02		5.700E-02	1.63E-05	3.86E-07
9.340E-02		5.700E-02	1.63E-05	3.86E-07
8.525E-02			1.66E-04	1.66E-06
8.525E-02			1.66E-04	1.68E-06
8.373E-02			1.63E-04	1.65E-06
8.373E-02			1.63E-04	1.52E-06
8.373E-02			1.63E-04	1.70E-06
8.901E-02			1.73E-04	1.46E-06
8.901E-02			1.73E-04	1.91E-06
8.901E-02			1.73E-04	2.25E-06
9.897E-02			1.92E-04	2.01E-06
9.897E-02			1.92E-04	2.04E-06
9.897E-02			1.92E-04	1.99E-06
9.392E-02			1.82E-04	1.68E-06
9.392E-02			1.82E-04	1.74E-06
9.392E-02			1.82E-04	1.80E-06
2.979E-02	3.666E-03		4.46E-04	6.13E-06
2.979E-02	3.666E-03		4.46E-04	6.45E-06
1.640E-02			2.45E-05	4.14E-07
1.640E-02			2.45E-05	4.47E-07
1.640E-02			2.45E-05	4.26E-07
1.897E-02	4.090E-04		4.37E-04	5.73E-07
1.897E-02	4.090E-04		4.37E-04	5.39E-07
9.431E-02		1.660E-04	1.82E-04	1.50E-06
9.431E-02		1.660E-04	1.82E-04	1.20E-06
9.431E-02		1.660E-04	1.82E-04	1.22E-06

APPENDIX B. (Continued)

$m_{S,\text{total}}/\text{mol kg}^{-1}$	$m_{\text{NaOH}}/\text{mol kg}^{-1}$	$m_{\text{HCl}}/\text{mol kg}^{-1}$	$m_{\text{H}_2(\text{aq})}/\text{mol kg}^{-1}$	$m_{\text{Au,total}}/\text{mol kg}^{-1}$
$t = 250^\circ\text{C}$				
4.900E-02			1.58E-04	1.02E-06
8.000E-02			1.58E-04	1.99E-06
8.000E-02	2.000E-01		4.28E-04	8.50E-05
7.400E-02	2.000E-01		4.29E-04	8.85E-05
7.100E-02		6.800E-02	7.85E-05	3.66E-07
7.100E-02		6.800E-02	7.85E-05	4.06E-07
8.800E-02		2.400E-01	7.87E-05	3.55E-07
8.800E-02		2.400E-01	7.87E-05	4.98E-07
9.340E-02		5.700E-02	1.63E-05	1.16E-06
9.340E-02		5.700E-02	1.63E-05	1.16E-06
9.887E-02			5.06E-04	1.76E-06
9.887E-02			5.06E-04	1.49E-06
1.226E-01			2.35E-04	2.51E-06
1.226E-01			2.35E-04	2.20E-06
1.306E-01			2.50E-04	2.03E-06
1.306E-01			2.50E-04	2.07E-06
1.306E-01			2.51E-04	2.40E-06
2.407E-02			2.36E-04	2.52E-07
2.407E-02			2.36E-04	2.97E-07
2.407E-02			2.36E-04	2.53E-07
2.194E-02	9.900E-04		2.24E-04	3.14E-06
2.194E-02	9.900E-04		2.24E-04	3.24E-06
2.194E-02	9.900E-04		2.23E-04	2.84E-06
2.758E-02	3.216E-03		2.32E-04	1.16E-05
2.758E-02	3.216E-03		2.32E-04	1.13E-05
2.758E-02	3.216E-03		2.31E-04	1.06E-05
3.323E-02	5.916E-03		2.40E-04	2.36E-05
3.323E-02	5.916E-03		2.39E-04	2.22E-05
3.323E-02	5.916E-03		2.40E-04	2.44E-05
6.279E-02	8.808E-03		2.57E-04	5.49E-05
6.279E-02	8.808E-03		2.57E-04	5.36E-05
6.279E-02	8.808E-03		2.58E-04	5.54E-05
$t = 300^\circ\text{C}$				
1.045E-01	8.300E-02		1.59E-04	3.01E-04
8.000E-02			1.58E-04	1.43E-06
8.000E-02			1.58E-04	1.69E-06
3.100E-02		4.300E-02	2.20E-04	2.61E-07
3.100E-02		1.000E-01	2.20E-04	2.76E-07
3.100E-02		1.000E-01	2.20E-04	2.16E-07
7.800E-02		1.000E-01	3.93E-04	4.12E-07
7.800E-02		1.000E-01	3.93E-04	3.51E-07
9.600E-02		1.000E-01	1.18E-04	8.35E-07
9.600E-02		1.000E-01	1.18E-04	9.46E-07
7.400E-02	2.000E-02		4.30E-04	9.46E-05
7.400E-02	2.000E-02		4.50E-04	1.16E-04
7.100E-02		6.800E-02	7.90E-05	1.11E-06
8.800E-02		2.400E-01	7.89E-05	8.60E-07
8.800E-02		2.400E-01	7.90E-05	1.11E-06
9.340E-02		5.700E-02	1.63E-05	3.00E-06
9.340E-02		5.700E-02	1.64E-05	3.15E-06
7.439E-02			3.80E-04	1.05E-06
7.439E-02			3.79E-04	8.05E-07
7.439E-02			3.79E-04	8.45E-07
1.107E-01			2.13E-04	1.76E-06
1.107E-01			2.13E-04	2.05E-06
1.107E-01			2.13E-04	1.80E-06
1.119E-01			2.15E-04	1.95E-06
1.119E-01			2.15E-04	2.38E-06
1.119E-01			2.15E-04	1.90E-06
1.124E-01			2.17E-04	2.55E-06
1.124E-01			2.16E-04	2.21E-06
1.110E-01			2.13E-04	1.90E-06
1.110E-01			2.13E-04	1.92E-06
1.110E-01			2.14E-04	1.99E-06
1.095E-01			2.10E-04	1.95E-06

APPENDIX B. (Continued)

$m_{S,\text{total}}/\text{mol kg}^{-1}$	$m_{\text{NaOH}}/\text{mol kg}^{-1}$	$m_{\text{HCl}}/\text{mol kg}^{-1}$	$m_{\text{H}_2(\text{aq})}/\text{mol kg}^{-1}$	$m_{\text{Au},\text{total}}/\text{mol kg}^{-1}$
1.095E-01			2.11E-04	2.19E-06
1.095E-01			2.11E-04	1.90E-06
4.625E-02	1.500E-02		5.99E-05	1.20E-04
4.625E-02	1.500E-02		6.21E-05	1.24E-04
4.625E-02	1.500E-02		5.92E-05	1.18E-04
4.830E-02	1.800E-02		5.25E-05	1.51E-04
4.830E-02	1.800E-02		5.12E-05	1.47E-04
4.830E-02	1.800E-02		5.17E-05	1.49E-04
4.830E-02	1.800E-02		5.02E-05	1.45E-04
5.662E-02	1.722E-02		5.94E-05	1.71E-04
5.662E-02	1.722E-02		5.77E-05	1.66E-04
5.662E-02	1.722E-02		6.25E-05	1.80E-04
5.662E-02	1.722E-02		6.21E-05	1.79E-04
4.613E-02	1.722E-02		6.90E-05	1.38E-04
4.613E-02	1.722E-02		6.75E-05	1.35E-04
4.613E-02	1.722E-02		6.57E-05	1.31E-04
4.613E-02	1.722E-02		6.48E-05	1.30E-04
4.298E-02	4.600E-04		3.34E-04	2.76E-06
4.298E-02	4.600E-04		3.34E-04	2.83E-06
4.298E-02	4.600E-04		3.34E-04	2.98E-06
2.443E-02	3.657E-03		3.43E-04	1.01E-05
2.443E-02	3.657E-03		3.45E-04	1.11E-05
2.443E-02	3.657E-03		3.45E-04	1.14E-05
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$t = 350^\circ\text{C}$				
1.045E-01	8.300E-02		1.45E-04	2.74E-04
1.045E-01	8.300E-02		1.36E-04	2.54E-04
1.328E-01	8.300E-02		3.20E-04	6.40E-04
8.000E-02			1.58E-04	2.09E-06
8.000E-02			1.58E-04	2.20E-06
3.100E-02		4.300E-02	2.20E-04	3.40E-07
3.100E-02		4.300E-02	2.20E-04	2.94E-07
3.100E-02		1.000E-01	2.20E-04	3.86E-07
7.400E-02	2.500E-02		4.59E-04	1.32E-04
7.400E-02	2.500E-02		4.60E-04	1.34E-04
9.340E-02		5.700E-02	1.63E-05	4.18E-06
9.340E-02		5.700E-02	1.64E-05	4.18E-06
4.767E-02	1.859E-02		3.59E-04	7.92E-05
4.767E-02	1.859E-02		3.60E-04	7.96E-05
5.005E-02	1.742E-02		1.77E-04	1.02E-04
5.005E-02	1.742E-02		1.88E-04	1.09E-04
8.528E-02	1.669E-02		2.43E-04	1.65E-04
8.528E-02	1.669E-02		2.38E-04	1.61E-04
4.400E-02	4.700E-04		3.32E-04	2.27E-06
4.400E-02	4.700E-04		3.32E-04	2.44E-06
4.400E-02	4.700E-04		3.32E-04	2.09E-06
2.440E-02	2.670E-03		3.39E-04	6.95E-06
2.440E-02	2.670E-03		3.44E-04	9.03E-06
2.440E-02	2.670E-03		3.42E-04	7.93E-06
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$t = 400^\circ\text{C}$				
1.328E-01	8.300E-02		2.22E-04	4.28E-04
8.000E-02			1.58E-04	1.04E-06
8.000E-02			1.58E-04	1.36E-06
3.100E-02		4.300E-02	2.20E-04	5.45E-07
3.100E-02		1.000E-01	2.20E-04	4.39E-07
3.100E-02		1.000E-01	2.20E-04	3.72E-07
9.600E-02		1.000E-01	1.18E-04	1.43E-06
9.600E-02		1.000E-01	1.18E-04	1.53E-06
7.400E-02	2.500E-02		4.62E-04	1.39E-04
7.400E-02	2.500E-02		4.61E-04	1.37E-04
9.340E-02		5.700E-02	1.63E-05	3.41E-06
9.340E-02		5.700E-02	1.64E-05	3.87E-06
6.714E-02	1.854E-02		1.23E-04	2.19E-04
6.714E-02	1.854E-02		1.30E-04	2.35E-04
6.656E-02	1.854E-02		1.19E-04	2.09E-04
8.388E-02	1.669E-02		1.52E-04	2.84E-04

APPENDIX B. (Continued)

$m_{S, total}/mol\ kg^{-1}$	$m_{NaOH}/mol\ kg^{-1}$	$m_{HCl}/mol\ kg^{-1}$	$m_{H_2(aq)}/mol\ kg^{-1}$	$m_{Au, total}/mol\ kg^{-1}$
8.388E-02	1.669E-02		1.49E-04	2.77E-04
7.703E-02	1.170E-03		1.85E-04	3.22E-05
7.703E-02	1.170E-03		1.85E-04	3.22E-05
6.410E-02	1.000E-04		2.40E-04	1.63E-06
6.410E-02	1.000E-04		2.40E-04	1.54E-06
3.220E-02	1.000E-04		2.57E-04	9.71E-07
3.220E-02	1.000E-04		2.57E-04	1.03E-06
$t = 450^{\circ}C$				
1.045E-01	8.300E-02		1.81E-04	3.45E-04
1.045E-01	8.300E-02		1.78E-04	3.40E-04
1.328E-01	8.300E-02		3.22E-04	6.45E-04
1.328E-01	8.300E-02		3.33E-04	6.65E-04
8.000E-02			1.58E-04	1.60E-06
8.000E-02			1.58E-04	1.68E-06
3.100E-02		4.300E-02	2.20E-04	6.40E-07
3.100E-02		4.300E-02	2.20E-04	6.19E-07
3.100E-02		1.000E-01	2.20E-04	7.29E-07
3.100E-02		1.000E-01	2.20E-04	5.24E-07
5.500E-02		1.000E-01	1.18E-04	1.21E-06
5.500E-02		1.000E-01	1.18E-04	1.01E-06
7.400E-02	2.000E-02		4.83E-04	1.44E-04
7.400E-02	2.000E-02		4.78E-04	1.37E-04
9.340E-02		5.700E-02	1.63E-05	4.09E-06
9.340E-02		5.700E-02	1.64E-05	4.65E-06
$t = 500^{\circ}C$				
1.045E-01	8.300E-02		2.02E-04	3.35E-04
8.000E-02			1.58E-04	2.34E-06
8.000E-02			1.58E-04	1.67E-06
8.000E-02			1.58E-04	1.36E-06
8.000E-02			1.58E-04	1.70E-06
3.100E-02		4.300E-02	2.20E-04	1.13E-06
3.100E-02		4.300E-02	2.20E-04	8.86E-07
3.100E-02		1.000E-01	2.20E-04	7.67E-07
3.100E-02		1.000E-01	2.20E-04	7.41E-07
7.400E-02	2.000E-01		5.92E-05	1.18E-04
7.400E-02	2.000E-01		7.46E-05	1.49E-04
9.340E-02		5.700E-02	5.28E-04	1.68E-06
9.340E-02		5.700E-02	5.43E-04	1.42E-06