The solubility of gold in water-hydrogen sulphide vapours: An experimental study

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ABSTRACT

This thesis presents the results of an experimental study of the solubility of Au in reduced sulphur-bearing vapours at elevated temperature and pressure, as well as the *PVTx* properties of H_2O-H_2S gas mixtures. The solubility of gold was measured in pure H_2S gas and H_2O-H_2S gas mixtures. Results of the experiments demonstrate that the fugacity of gold increases with the fugacity of H_2S , and that reactions involving the formation of volatile sulphide species control the solubility of gold in the gas phase. The results obtained for pure H_2S gas indicate that solvation of sulphide gold species by molecules of H_2S significantly increases the dissolution of gold, whereas the experiments with H_2O-H_2S vapour mixtures showed that this dissolution is further enhanced by hydration of the gold sulphide. The following reactions are interpreted to control the solubility of gold in H_2O-H_2S gas mixtures:

$$Au(s) + (n+1)H_2S(g) = AuS \cdot (H_2S)_n(g) + H_2(g)$$

$$Au(s) + H_2S(g) + mH_2O(g) = AuS \cdot (H_2O)_m(g) + H_2(g)$$

Equilibrium constants and the solvation or hydration numbers (*n* or *m*) for these reactions were determined by minimizing the errors between the results for an optimized solvation/hydration model and the experimental data. The fugacity of H_2S and H_2O required for the model calculation were determined from the experimentally determined *PVTx* properties of the H_2O - H_2S fluid mixtures; the latter were modeled using cubic equations of state with composition- and density-dependent mixing rules and adjusted binary interactions parameters.

Under the experimental conditions of this study, i.e., temperatures from 300 to 400 °C, pressures up to 265 bar, and hydrogen fugacity constrained by the reaction $H_2+S=H_2S$, the solubility of gold in reduced sulphur-bearing vapour is relatively high (up to 1 ppb), and the results obtained provide strong evidence that H_2S plays an important role in the vapour transport of gold. As most natural hydrothermal vapours are water rich (>90% H₂O), gold will be transported in the vapour dominantly as an hydrated gold sulphide, provided that there is sufficient reduced sulphur (H₂S) in the vapour for complexation. The stoichiometry and stability of the gold complexes determined in this study represent an important contribution to our knowledge of the chemical properties of volatile metal species and permit accurate modeling of vapour-related processes involved in the mobilization, transport and deposition of gold in magmatic hydrothermal systems, notably those of epithermal environments.

RESUME

Cette thèse présente les résultats d'une étude expérimentale sur la solubilité de l'or dans des vapeurs contenant du souffre à l'état réduit à haute pression et température, ainsi que les propriétés *PVTx* de mélanges gazeux de H_2O-H_2S . La solubilité de l'or a été mesurée dans du H_2S gazeux pur et dans des mélanges gazeux de H_2O-H_2S . Les résultats de cette expérience démontrent que la fugacité de l'or augmente avec la fugacité de H_2S , et que les réactions qui mènent à la production d'espèces volatiles de souffre contrôlent la solubilité de l'or dans la phase gazeuse. Les résultats obtenus pour le gaz de sulfure d'hydrogène à l'état pur indiquent que la solvatisation des espèces de sulfure d'or par les molécules de sulfure d'hydrogène augmente de façon significative la dissolution de l'or, alors que les résultats issus des expériences utilisant des mélanges gazeux de H_2O et de H_2S montrent que cette dissolution est davantage augmentée par l'hydratation du sulfure d'or. Nous proposons que les réactions suivantes contrôlent la solubilité de l'or dans des mélanges de H_2O-H_2S :

$$Au(s) + (n+1)H_2S(g) = AuS \cdot (H_2S)_n(g) + H_2(g)$$
$$Au(s) + H_2S(g) + mH_2O(g) = AuS \cdot (H_2O)_m(g) + H_2(g)$$

Les constantes d'équilibre ainsi que le degré de solvatisation ou d'hydratation (n ou m) pour ces réactions furent déterminés par minimisation de l'erreur entre les résultats obtenus d'un modèle de solvatation/hydratation optimisé et les données expérimentales. Les fugacités de H₂S et de H₂O requises pour les calculs du dit modèle furent établies en utilisant les propriétés de *PVTx* expérimentalement déterminées pour les mélanges fluides de H_2O-H_2S ; ces dernières furent modélisées en utilisant des équations d'état cubiques avec des lois de mélange sur la dépendance de composition et densité, ainsi que des paramètres sur les interactions binaires spécialement ajustées.

Dans les conditions de cette étude, c'est- à -dire à 300-400 °C et à des pressions jusqu'à 265 bars, la fugacité de l'hydrogène étant contrainte par la réaction chimique H₂+S=H₂S, la solubilité de l'or dans des vapeurs de soufre à l'état réduit est relativement élevée (jusqu'à 1 ppb), et les résultats démontrent que le sulfure d'hydrogène joue un rôle important dans le transport de l'or par la vapeur. La plupart des vapeurs hydrothermales dans la nature sont riches en eau (>90% H₂O), donc l'or sera transporté par la vapeur sous la forme de sulfure d'or hydraté si il y a assez de sulfure d'hydrogène à l'état réduit pour qu'il y ait complexation. La stœchiométrie et la stabilité des complexes d'or déterminés dans cette étude représentent une contribution essentielle à la caractérisation des propriétés chimiques sur les espèces métalliques volatiles et permettent une modélisation précise des processus à l'état vapeur et inhérents à la mobilisation, le transport et le dépôt de l'or dans des systèmes hydrothermaux magmatiques, en particulier les environnements épithermaux.

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LIST OF SYMBOLS

- P pressure (bar)
- T-temperature
- R gas constant (83.14 cm³ bar K⁻¹ mol⁻¹)
- V volume (cm³)
- v_i partial molar volume of component *i*
- ρ density
- f-fugacity
- φ_i fugacity coefficient of component *i* in a gas mixture
- a_i activity of component *i* in an aqueous liquid
- γ_i activity coefficient of component *i* in an aqueous liquid
- N- number of moles
- N^{liq} total number of moles in the liquid
- N^{vap} total number of moles in the vapour
- x_i mole fraction of component *i* in the liquid
- y_i mole fraction of component *i* in the vapour
- $\varphi^0_{H_2O}$ fugacity coefficient of pure H₂O at saturation with liquid
- $P_{H_2O}^{\nu p}$ vapour pressure of pure H₂O at saturation with liquid
- $K_{H,S}(T,P)$ Henry's law constant at a specified temperature and pressure
- n solvation number
- m hydration number
- k_{ij} and c_{ij} binary interaction parameters of the equation of state

PREFACE (Contribution of Authors)

This thesis presents the results of an experimental investigation conducted in the Department of Earth and Planetary Sciences, McGill University. It comprises, in large part, three manuscripts submitted to the journal, Geochimica et Cosmochimica Acta. Aspects of this study were also presented and discussed at the international Goldschmidt conferences between 2007 and 2010. Chapter 2 was published in 2007, at an early stage of the research; Chapters 3 and 4 were submitted later. All manuscripts were initiated through a collaboration involving the author, his advisor, Professor A.E. Williams-Jones, and co-supervisor Dr. A.A. Migdisov. Professor A.E. Williams-Jones, who inspired the vapour-transport experimental project, contributed greatly to the development of the research approach, interpretation of the results and preparation of the publications. Dr. A.A. Migdisov was involved in the development of the experimental procedure, guided the thermodynamic interpretation of results and also contributed to the revision of the manuscripts. The bulk of the analyses of experimental samples (instrumental neutron activation, INAA) were performed at Ecole Polytechnique (University of Montreal); some control and supplementary analyses were performed at McGill University (Geochemical Laboratories) and the Geoscience Laboratories (Sudbury, Ontario). The author conducted all of the experimental work (at McGill University) and performed the thermodynamic calculations that were required to interpret the results. He was responsible for all data treatment and publication of the research findings.

Chapter 1

General introduction

1.1. VAPOUR TRANSPORT OF METALS

There is general agreement that high-temperature high-density aqueous fluids are responsible for local enrichments of ore elements in the upper crust of several orders of magnitude. Nevertheless, this does not preclude the possibility that other fluids may also play a role in metal transport. Indeed, this may be the case for magmatic-related hydrothermal systems sourced by shallowly emplaced intrusions and exemplified by porphyry and epithermal deposits. The formation of these economically important deposits of Cu, Au, Ag and other metals has generally been attributed to hydrothermal mobilization of ore components by saline aqueous liquid (Burnham, 1979; Hedenquist and Lowenstern, 1994). Nonetheless, pressure-temperature conditions favour the existence of vapour in many magmatic hydrothermal ore-forming systems, due either to direct subcritical exsolution of this phase and liquid from the melt (Bodnar et al., 1985; Williams-Jones and Heinrich, 2005) or its later separation from a single fluid phase (Drummond and Ohmoto, 1985). Moreover, there is evidence that, in some cases, the vapour may constitute as much as 90% of the bulk fluid by mass (Hedenguist et al., 1998; Landtwing et al., 2010). It is thus reasonable to consider the possibility, as some researchers have done (e.g., Henley and McNabb, 1978; Eastoe, 1982; Sillitoe, 1983; Symonds et al., 1987; Giggenbach, 1992; Heinrich et al., 1992; Williams-Jones et al., 2002), that vapour may also be important in mobilizing metals.

Until recently, it had been assumed that the role of the vapour in magmatic hydrothermal systems is only to control redox and other physicochemical conditions. For example, boiling, a commonly occurring process in porphyry and epithermal

environments, is widely considered to promote deposition of ore metals from the aqueous liquid by removing volatile gaseous species (Drummond and Ohmoto, 1985; Reed and Spycher, 1985; Brown, 1989). This is because: 1) in many cases, the gases are acidic (e.g., CO_2 , HCl, H_2S) and their loss makes the residual liquid more alkaline; and 2) in some cases, the gas is a ligand (e.g., H_2S). The possibility that the vapour may play a role in metal transport has been largely ignored, despite several publications proposing it in the modern era. One of the earliest of these publications was by Brown (1948a) which, based on observations of blast furnace smelting, concluded that the occurrence of zoning in sulphide ore deposits reflects the differential volatility of sulphide minerals. Brown (1948a, b) proposed that volatile sulphide species are the principal agents of metal transport during the formation of sulphide ore deposits. Later, Walker and Walker (1956) proposed that volatile chloride species may also be involved in the transport of metals. These proposals were not adopted, largely because of calculations by Krauskopf (1957, 1964) based on the volatility of metals and metallic minerals. His calculations showed that the volatility of most metals is significant only at temperatures over 600 $^{\circ}$ C, and the volatility of copper, silver and gold and the sulphides and chlorides of these metals is so low as to preclude transport by vapour under any conditions that might occur in nature.

The vapour theory of metal transport was revisited by Henley and McNabb (1978) who proposed the vapour plume model for Cu-Mo porphyry deposit genesis. Nevertheless, with few exceptions (e.g., Eastoe, 1982; Sillitoe, 1983; Symonds et al., 1987; Giggenbach, 1992), the notion that vapour could constitute an ore fluid did not gain traction.

The first direct evidence of the ability of vapours to transport metals came from analyses of volcanic gases, sublimates and incrustations (e.g., Zambonini, 1910; Zeis, 1924 and 1929; Pelloux, 1927; Naboko, 1959; Stoiber and Rose, 1974; Symonds et al., 1987, Hedenquist et al., 1994; Taran et al., 1995; Williams-Jones et al., 2002). These analyses (which for a long time were ignored by the economic geology community), together with calculations suggesting that vapour may be present in greater proportions than liquid during the evolution of magmatic hydrothermal systems and related ore formation, encouraged a number of researchers to quantitatively assess the ability of vapours to transport metals (e. g., Symonds, 1987; Spycher and Reed, 1989; Symonds and Reed, 1993). Using volcanic gases and the vapour phase in geothermal systems as analogues of hydrothermal fluids, these researchers evaluated the vapour transport hypothesis by applying available thermodynamic data for volatile metallic species. However, these calculations suffered because of a lack of reliable data for these species and failed to provide convincing evidence that vapours can transport metals in concentrations sufficient to form economic deposits.

With advances in micro-analytical techniques, vapour-rich fluid inclusions containing high concentrations of metals were discovered (e.g., Heinrich et al., 1992 and 1999; Ulrich et al. 1999; Baker et al., 2004; Williams-Jones et al., 2005; Pudack et al., 2009; Seo et al., 2009; Zajacz and Halter, 2009; Landtwing et al., 2010). The most surprising results were for copper and gold, which showed that these metals partition preferentially into the vapour over the coexisting brine and, in some cases, may reach concentrations up to 3 wt.% and 10 ppm, respectively (e.g., the Grasberg porphyry deposit, Indonesia; Ulrich et al., 1999). In addition to analyses of vapour-rich fluid

inclusions, some textural features, such as the presence of euhedral quartz crystals in sulphosalts, crystal-lined vugs and distinct textural domains of intergrowths in high-sulphidation enargite-gold deposits suggested formation of the latter from a vapour (e.g., the experimental study of vapour-melt systems by Mavrogenes et al., 2010).

The concentration of gold in the magmatic volatile phase may exceed its concentration in the source melt by up to several orders of magnitude (Audetat et al., 2000; Audetat and Pettke, 2003; Ulrich et al., 1999; Mustad et al., 2006). This, the large amount of a vapour that can be exsolved from a magma body (Henley and McNabb, 1978; Williams-Jones and Heinrich, 2005), the preference of gold for vapour over liquid and the longevity of many magmatic-hydrothermal systems (> 10^5 years; Page and McDougall, 1972; Arribas et al., 1995; Parry et al., 2001), provide strong arguments that the vapour is the principal mode of transport in many magmatic-hydrothermal oreforming systems.

In order to adequately model processes of ore formation involving vapour, a better understanding of the mechanisms of metal dissolution in the vapour is required. Theoretical approaches based on the volatility of gold, gold sulphide or chloride solids are incapable of explaining the observed high concentrations of gold in natural vapours. It is therefore necessary to seek new approaches involving the formation of stable volatile metal species and solvation (Sourirajan and Kennedy, 1962; Martynova, 1964; Styrikovich, 1969; Galobardes et al., 1981; Bischoff and Rosenbauer, 1986; Alekhin and Vakulenko, 1987; and Armellini and Tester, 1993; Migdisov et al., 1999; Archibald et. al, 2001 and 2002; Zakaznova-Iakovleva et al., 2002; Migdisov and Williams-Jones, 2005; Rempel et al., 2006, 2008 and 2009).

Interestingly, over sixty years ago, Brown (1948a) first suggested that metals, such as gold and silver, may react ("attach themselves") to volatile sulphur, selenium or tellurium "for the journey". Although the reaction mechanisms and thermodynamic properties of volatile metal species are still not completely understood, it is now known that gas-phase reactions involving the formation of metal-bearing complexes may occur due to molecular bonding, both ionic and low-energy (van der Waals) interactions. The latter can lead to the formation of solvation shells, which can (potentially) increase the solubility of metals in the vapour phase. However, quantitative evaluation of these phenomena, and more particularly the speciation and stability of metallic complexes in the vapour requires the accumulation of a body of reliable experimental data for conditions encountered in nature.

1.2. EXPERIMENTAL STUDIES OF THE SOLUBILITY AND SPECIATION OF METALS IN VAPOURS

The ability of gases to dissolve solids has been investigated experimentally since the end of the nineteenth century (e.g., Hannay and Hogarth, 1879). Most of the early investigations, results of which are summarized in Morey and Ingerson (1937) and Morey (1957), focused on the solubility of salts of alkali and alkali earth metals, silica and silicate minerals in water vapour. It was not until 1951 that the first experimental study involving the solubility of ore minerals was published. This study (Morey and Hesselgesser, 1951) investigated the solubility of Cu and Fe sulphide and oxide minerals

in water vapour (superheated steam) by passing a flow of water steam over them at temperatures up to 600 °C and pressures up to 2000 bar, condensing the steam to liquid and then analysing the condensed liquid and mineral precipitates. The solubility of sulphides was found to be extremely low compared to that of silicate and sulphate phases. Subsequent experimental studies of the solubility of metal oxides in water vapour by Pocock and Stewart (1963; Cu, Fe and Co) and Gotsiridze (1969; Fe, Co and Ni) showed that their solubility in superheated steam (at temperatures of ~510-620 °C and 350 to 500 °C, respectively) is a function of pressure and depends on the specific volume (density) of the steam.

As theories of hydrothermal ore deposit formation, until recently, all assumed transport of the metals by the aqueous liquid (e.g., Lindgren, 1933; Graton, 1940; Bateman, 1950; Holland, 1972; Burnham, 1979; Guilbert and Park, 1986), most experimental solubility and speciation studies during the past 60 years have been conducted with aqueous liquids (summarized in Barnes, 1997; Wood and Samson, 1998). Further experimental studies of the solubility of metals in the gas phase were effectively discouraged until the discovery of vapour inclusions containing high concentrations of metals in the 1990's (see above). The lack of data on the stability of ore metal-bearing gaseous compounds at hydrothermal conditions and the newly apparent need for such data led to a series of experimental studies on the solubility of metals in the vapour phase at elevated temperatures and pressures (see Williams-Jones et al., 2002 and references therein; Williams-Jones and Heinrich, 2005; Migdisov and Williams-Jones, 2005). These studies showed that metals could be dissolved in the vapour phase via gas-phase

reactions, leading to the formation of new stable complexes, or by solvation/hydration processes similar to those operating in aqueous liquid.

As chloride complexes can control the solubility of Au in acidic aqueous liquid solutions at temperatures above 300 °C (e.g., Seward, 1973; Zotov et al., 1991; Stefansson and Seward, 2004) and HCl is one of the dominant components in natural magmatic vapours (evident from the analyses of volcanic gases; see Symonds et al., 1994; Williams-Jones et al, 2005; Webster and Mandeville, 2007), the first modern experiments dealing with the solubility of gold in vapour were in the system H₂O-HCl (Archibald et al., 2001). In order to extract reliable thermodynamic data for modeling multicomponent systems containing vapour, the experiments were performed in the liquid-undersaturated system at temperatures below 360 °C. The theoretical model employed in the investigations is analogous to that developed for the description of the solubility of NaCl in water vapour. The latter model successfully explained the enhanced solubility of halite in water vapour (the solubility exceeded that predicted from volatility data by several orders of magnitude; Styrikovich, 1969; Martynova, 1964; Sourirajan and Kennedy, 1962; Galobardes et al., 1981; Bischoff and Rosenbauer, 1986; Alekhin and Vakulenko, 1987; and Armellini and Tester, 1993). According to this model, the solubility of metal in the vapour is controlled not only by the formation of stable simple gaseous compounds (e.g., NaCl^{gas}), but also by the formation of solvated complexes (NaCl $(H_2O)_n$) as a result of low-energy electrostatic interactions of metallic species with the gas-solvent.

Currently, there are no data available for the complexation of gold with reduced sulphur in water vapour. Inasmuch as H₂S is an important constituent of natural magmatic fluids (e.g., Hedenquist and Lowenstern, 1994; Heinrich et al., 1999; Williams-Jones and Heinrich, 2005), partitions strongly into vapour relative to liquid in magmatichydrothermal systems (Drummond, 1981; Drummond and Ohmoto, 1985; Gammons and Williams-Jones, 1995), and forms very stable aqueous complexes with gold either as HS⁻ or H₂S (e.g., Shea and Helz, 1988; Hayashi and Ohmoto, 1991; Benning and Seward, 1996; Zotov et al., 1996; Loucks and Mavrogenes, 1999; Stefansson and Seward, 2004; Tagirov et at., 2005; Pokrovski et al., 2009a), complexation with H₂S is an obvious candidate to explain the elevated concentrations of Au in the vapour phase of natural magmatic hydrothermal systems.

Several experimental studies have recently investigated the partitioning of gold into the vapour phase (Simon et al., 2007; Pokrovski et al., 2008; Zajacz et al., 2010). The experiments of Simon et al. (2007) and Zajacz et al. (2010) focused on the vapour-melt partitioning of Au at magmatic conditions (800 °C, 1200 bar and 1000 °C, 1500 bar, respectively) and came to contradictory conclusions. Simon et al. (2007) found the presence of H₂S to have a relatively insignificant effect on the partitioning of gold into the vapour and, therefore, on the scavenging of gold from the rhyolite melt. In contrast, Zajacz et al. (2010) showed in experiments with synthetic fluid inclusions in quartz, that bisulphide complexes of gold prevail over chloride complexes in a low-density vapourlike phase. Moreover, they found that alkali chlorides (NaCl, KCl, LiCl, CaCl₂) enhance the solubility of gold in H₂S-bearing vapours. Pokrovski et al. (2008) estimated the vapour-liquid partitioning of gold and other metals at temperatures up to 500 °C for water-salt (±sulphur) systems. They found that the addition of 1-3 wt.% of S to the system increased the equilibrium distribution coefficient ($K_m = m^{vapour}/m^{liqud}$) for gold by a factor of 100, allowing for its preferential partitioning into the vapour by up to 10 times (K_m =1-10). One interpretation is that this implies the formation of volatile complexes of gold with reduced sulphur ligands in the vapour due to solute-solvent interactions. These experimental studies only provided a qualitative assessment of the solubility of gold in the vapour and the contribution of sulphur to this solubility. They did not provide any information on the stability and stoichiometry of the gold complexes, something that is essential for numerical modeling of gold transport and deposition in vapour-dominated hydrothermal systems.

Recent advances in synchrotron radiation techniques coupled with spectroscopic analysis of fluids make X-ray absorption spectroscopy (XAS) a powerful method for determining the speciation of metals in high-temperature fluids. A number of XAS studies of Cu complexes have been conducted on the fluids from natural fluid inclusions (Mavrogenes et al., 2002; Cauzid et al., 2007; Metrich et al., 2009). These studies, together with PIXE and ICPMS analyses (Heinrich, 1992 and 1999; Ulrich et al., 1999; Baker et al, 2004), have revealed that copper behaves similarly to gold in hydrothermal systems and partitions preferentially into the vapour. As ICPMS analyses of vapour inclusions suggest that the solubility of copper in the vapour may reach wt.% levels (Ulrich et al., 1999; Seo et al., 2009), this metal has become an attractive target for experimental studies applying XAS to vapours. Using this method (XANES and EXAFS), Etschmann et al. (2010) investigated the speciation and solubility of Cu(I) chloride and sulphide complexes in experimental aqueous vapours and liquids at temperatures up to ~ 600 °C and pressures up to 600 bar. They found that the predominant species in the vapour is similar to that in the liquid, and likely has a stoichiometry $Cu(HS)(H_2S)^0$. However, the preferential partitioning of copper into a vapour relative to

liquid was not observed in these experiments, and the levels of concentration of Cu in the vapour were significantly lower than measured in fluid inclusions (0.06 wt.% of Cu in the experiments versus >1 wt.% in natural fluid inclusions).

The structure and stability of Au species in Cl- and S-bearing aqueous liquids have been investigated using XAS methods at temperatures up to 500 °C and pressures up to 600 bar (Pokrovski et al., 2009 a, b). However, the sensitivity of this approach is currently not sufficient to study the complexation of gold in the vapour. Also, as mentioned by Pokrovski et al. (2009a), a solvation shell of gold complexes with sulphur ligands is hard to detect unambiguously in the fluid. Therefore, autoclave-based experimental methods involving measurements of the solubility of gold in different solvents at a variety of ligand concentrations are still the only appropriate means for establishing the speciation of this metal in low-density vapour-like fluids.

The objectives of this thesis were to investigate the role of H_2S and sulphide complexation of gold on the solubility of this metal and its transport in the vapour phase at conditions relevant to the formation of porphyry and epithermal hydrothermal deposits. As a first step, the solubility of gold was studied in pure hydrogen sulphide in order to establish the interactions of the metal with reduced sulphur in the relatively simple H-S-Au system, and in turn, determine the speciation and stability of gold complexes in the gas phase. Gold solubility experiments were subsequently conducted in H_2O-H_2S gas mixtures to evaluate the speciation of gold in the more complex gas-only system H-O-S-Au, as well as estimate the relative importance of hydration (by H_2O molecules) and solvation (by H_2S molecules) processes in vapours of composition similar to those of natural low-density magmatic-hydrothermal fluids.

1.3. THE PROPERTIES OF H2O-H2S FLUID MIXTURES

In order to quantitatively evaluate the solubility and speciation of gold in H_2O-H_2S gas mixtures, it is necessary to accurately know the properties of the water-hydrogen sulphide system. This system is of great importance for studying many processes occurring in geological settings. Most of the magmatic-hydrothermal, metamorphic and geothermal fluids in the crust contain hydrogen sulphide or products of its dissociation. Knowledge of the properties of H_2S -bearing liquids and vapours is essential to evaluate the involvement of these fluids in the mobilization and deposition of metals in nature and in the experiments.

Unfortunately, there are no data available for modeling and calculating the *PVTx* properties of the system H₂O-H₂S at temperatures and pressures occurring in the crust. As geochemical investigations have focussed mainly on aqueous liquids, most published experimental studies of the H₂O-H₂S system have dealt with the solubility of hydrogen sulphide in water and salt solutions. Determining Henry's constant for H₂S was the main objective of these studies (Winkler, 1906; Wright and Maas, 1932; Selleck et al., 1952; Kozintseva, 1964; Clarke and Glew, 1971; Lee and Mather, 1977; Drummond, 1981; Gillespie and Wilson, 1982; Barret et al., 1988; Suleimenov and Krupp, 1994). Owing to the extremely corrosive nature of hydrogen sulphide, the experimental data were obtained at low temperatures (mostly under 200 °C, with a few studies reaching 330 °C) and low partial pressures of H₂S. Data on the properties of the vapour, with rare exceptions (Gillespie and Wilson, 1982), were not reported for these mixtures.

The H_2O-H_2S system is also of great interest in the field of chemical engineering, where the properties and behaviour of fluid mixtures must be accurately determined for the processing of oil and natural gas, petroleum reservoir engineering, geothermal energy, hydrometallurgy and the production of heavy water. Most of these applications are for low temperature and consequently most of the studies that have investigated the behaviour of H_2O-H_2S gas mixtures have focused on the low-temperature part of the system.

At the conditions of interest for magmatic-hydrothermal processes, water and hydrogen sulphide exhibit a strong non-ideal mixing behaviour, because of the polar nature of the molecules and hydrogen bonding in the fluid. Molecular interactions in H_2O-H_2S mixtures significantly affect both liquid and vapour phases, precluding the use of simple one-fluid models based on a single equation of state for the calculations of vapour-liquid equilibrium and the properties of the phases. Thus, to perform calculations involving water and hydrogen sulphide, such as accurately modelling processes in high-temperature fluids, and calculating the distribution and solubility of elements in vapour and liquid in natural and experimental systems, comprehensive thermodynamic models and/or equations of state are required to describe the non-ideality of the fluid mixtures. Experimental data are needed to constrain the behaviour of H_2O-H_2S fluids and model the H_2O-H_2S system at elevated temperatures and pressures.

An important objective of this thesis was to determine the volumetric properties of a H_2O-H_2S fluid mixtures and model the corresponding system. Experimental data on the *PVTx* properties of these mixtures were obtained in both the vapour-only and vapourliquid regions at temperatures up to 400 °C. Pressure measurements in this corrosive

mixture of fluids were made using a custom-designed pressure transducer. Based on the resulting experimental data, an equation of state to evaluate the properties of the vapour phase was implemented, and an asymmetric model describing vapour-liquid equilibrium in the system based on this equation of state was proposed to constrain a phase diagram for H_2O-H_2S fluid mixtures at elevated temperature and pressure.

1.4. THESIS ORGANIZATION

This thesis consists of 5 chapters: a general introduction, three manuscript-based chapters and a general conclusion. Two chapters present the results of experimental investigations of the solubility and speciation of gold in hydrogen sulphide-bearing vapours. The set of conditions in the experiments was guided by the observation that gold is one of two metals known to partition strongly into the vapour phase in natural systems, e.g., porphyry and epithermal ore forming systems. The strong affinity of gold to reduced sulphur ligands and its occurrence in sulphide ore deposits imply significant dissolution and mobilization of gold in the vapour, the phase commonly dominating in the abovementioned hydrothermal settings. The first manuscript (Chapter 2) addresses the complexation of gold with reduced sulphur in hydrogen sulphide gas and assesses the possible solvation of sulphide species in the experiments and in natural fluids.

The third chapter reports the results of the experimental determination of the PVTx properties of the H₂O-H₂S system and provides the equation of state and thermodynamic model required for the calculation of vapour-liquid equilibrium, as well as the properties of homogeneous vapour mixtures. The mixing rules and binary interaction parameters for

cubic equations of state considered in this paper permit accurate calculation of the fugacity of components in H_2O-H_2S vapour mixtures. Thus, the third chapter provides an essential tool for the evaluation of the solubility and speciation of gold in the mixtures of H_2O and H_2S gases reported in Chapter 4.

The fourth chapter is based on the same experimental approaches and modeling calculations as Chapter 2. The modeling procedure was originally developed for the study of the H₂O-NaCl system, and was successfully applied in the recent studies of the solubility of metals in the gas phase (cf. Williams-Jones and Heinrich, 2005; Rempel et al., 2006 and 2008; Kruszewski and Wood, 2009). The solubility and possible stoichiometry of complexes of gold with reduced sulphur were determined at temperatures from 300 to 360 °C and pressures up to ~260 bar. The solvation and hydration of gold sulphide complexes by several molecules of H₂S or H₂O are considered to account for the enhanced solubility of gold in the experimental gaseous mixtures. A comparison is made of the effects of sulphide and chloride complexation in the vapour phase in the context of the dissolution and transport of gold during the evolution of shallowly degassing magmatic intrusions.

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INTRODUCTION TO CHAPTER 2

Results of the historical review of natural observations and experimental studies presented in Chapter 1 support the theory of the vapour transport of metals, including gold, in hydrothermal systems. Nevertheless, satisfactory interpretation of the solubility of gold in natural fluids is still not possible because of the paucity of data on the speciation and stability of volatile complexes of gold. The thermodynamic database for gaseous gold species is limited to data for molecular Au or chloride species and these are insufficient to account for the solubility of gold at hydrothermal conditions. Owing to the known affinity of gold for reduced sulphur, sulphide species may also play a role in the stabilization of gold in hydrothermal vapour.

The results of an experimental study of the complexation of gold with reduced sulphur, mainly hydrogen sulphide, are presented in Chapter 2. The nature and stability of solvated sulphide species were investigated at elevated temperatures and pressures in supercritical H₂S gas. The stoichiometry of the gaseous gold complex was determined from solubility measurements conducted over a range of the gas-solvent fugacities. The complexation of gold as a solvated sulphide species is compared with that of hydrated chloride species at similar physicochemical conditions. Based on this comparison, the capacity of vapours to dissolve gold in natural settings is discussed.

Chapter 2

The solubility of gold in hydrogen sulphide gas: An experimental study

Denis Yu. Zezin, Artashes A. Migdisov, Anthony E. Williams-Jones

2.1. ABSTRACT

The solubility of gold in H_2S gas has been investigated at temperatures of 300, 350 and 400 °C and pressures up to 230 bar. Experimentally determined values of the solubility of Au are 0.4 to 1.4 ppb at 300 °C, 1 to 8 ppb at 350 °C and 8.6 to 95 ppb at 400 °C. Owing to a positive dependence of the logarithm of the fugacity of gold on the logarithm of the fugacity of H_2S , it is proposed that the solubility of Au can be attributed to the formation of a solvated gaseous sulphide or hydrosulphide complex through reactions of the type:

$$Au(s) + (n+1)H_2S(g) = AuS \cdot (H_2S)_n(g) + H_2(g),$$
(A1)

or

$$Au(s) + (n+1)H_2S(g) = AuHS \cdot (H_2S)_n(g) + 0.5H_2(g),$$
(A2)

which are f_{H_2} -dependent; *n* is a statistical solvation number. If the redox potential is buffered by S/H₂S (the case in our study), the corresponding reactions are:

$$Au(s) + nH_2S(g) + S(l) = AuS \cdot (H_2S)_n(g),$$
 (A3)

or

$$Au(s) + (n+0.5)H_2S(g) + 0.5S(l) = AuHS \cdot (H_2S)_n(g)$$
(A4)

Values of *n* for these latter reactions were calculated to be 1.8 and 1.2 at 300 °C, 1.7 and 1.0 at 350 °C, 2.2 and 1.7 at 400 °C, respectively. The equilibrium constants for reactions A3 and A4 increase with temperature and have values of log $K = -11.1 \pm 0.2$ at 300 °C

(both reactions), -10.7 ± 0.3 and -10.5 ± 0.3 at 350 °C, and -10.6 ± 0.2 and -10.4 ± 0.2 at 400 °C, respectively. At the conditions of this study, the solubility of gold in H₂S gas is relatively high, and the results obtained provide strong evidence that H₂S can play an important role in the vapour transport of gold and the formation of hydrothermal gold deposits.

2.2. INTRODUCTION

Although there is now extensive evidence that the vapour phase in magmatic hydrothermal systems is capable of transporting high concentrations of some ore metals (see review in Williams-Jones and Heinrich, 2005), our understanding of how this transport occurs is still poor. The first experimental study to address this issue was that of Migdisov et al. (1999) who showed that at temperatures from 300 to 360 °C and pressures up to 180 bar, the solubility of silver in H₂O-HCl vapours is orders of magnitude higher than predicted by simple volatility. They related this enhanced solubility to the formation of the species $AgCl(H_2O)_n$. Archibald et al. (2001; 2002) reported even higher solubilities of gold and copper in H₂O-HCl vapours at similar conditions and likewise interpreted their data as reflecting the formation of hydrated chloride complexes $(AuCl (H_2O)_n$ and $Cu_x Cl_x (H_2O)_n$). These latter studies measured concentrations of copper and gold in the vapour phase on the order of hundreds of ppm ($\mu g/g$) and tens of ppb ($\mu g/kg$), respectively, at a temperature of ~ 300 °C. In contrast, Heinrich et al. (1992 and 1999) measured weight percent and ppm level concentrations of these metals, respectively, in higher temperature (>550 °C) vapour-rich fluid inclusions from magmatic ore deposits. Moreover, they showed that both metals partition preferentially into the vapour phase rather than into the coexisting brine. Based on this observation (i.e., that the concentrations of the metals do not correlate with chloride activity) and the fact that H₂S has a strong preference for the vapour phase, these authors proposed that the high concentrations of copper and gold in the vapour phase are due to their complexation with reduced sulphur.

The only experimental study to shed direct light on the ability of H₂S to complex with metals in the vapour phase is that of Zakaznova-Iakovleva et al. (2001), who showed that H₂S gas can dissolve significant concentrations of antimony as a result of the formation of the solvated species Sb_2S_3 · H_2S . More recently, Pokrovski et al. (2006) have shown that the presence of sulphur may increase the partitioning of Au, Ag and Cu into the vapour phase at temperatures of up to 450 °C.

Inasmuch as complexes with HS⁻ and H₂S are the principal forms of dissolved gold in aqueous liquids (e.g., Hayashi and Ohmoto, 1991; Benning and Seward, 1996; Loucks and Mavrogenes, 1999; Stefansson and Seward, 2004; Tagirov et at., 2005) and H₂S partitions strongly into the vapour phase of hydrothermal systems, it is also likely that gaseous H₂S is an essential component in promoting the volatile transport of gold. In this paper, we report the results of an experimental study of the solubility of gold in hydrogen sulphide gas, and show that gold forms stable complexes with H₂S that greatly increase its solubility over that predicted by the vapour pressure of metallic gold or even more volatile species like AuS. This study represents a first step towards understanding the behaviour of gold in H₂S-bearing gases and is an essential step towards the quantitative modeling of gold transport and deposition in vapour-dominated hydrothermal systems.

2.3. METHOD

The method used in this study is identical to that described in previous experimental studies devoted to the transport of metals in the gas phase (e.g., Migdisov et al., 1999; Archibald et al., 2001; 2002; Zakaznova-Iakovleva et al., 2001; Migdisov and Williams-Jones, 2005; Rempel et al., 2006). The experiments were carried out in titanium-alloy autoclaves (Grade 2 and VT1-0) with volumes of ~40-50 cm³. Autoclave volumes were determined by filling the autoclaves with distilled water at 25 °C, and weighing them before and after filling. The weighing was performed to an accuracy of ±10 mg. Due to a thermal expansion, the volume of the autoclave could have increased by 0.8-1% at temperatures of 300-400 °C, imposing an additional uncertainty on the measured value. After the autoclaves had been purged of atmospheric gases by passing nitrogen gas through them for about 30 minutes, they were cooled to a temperature of approximately - 75 °C, and between 1 and 6 g of liquid H₂S was condensed in them from a stream of H₂S gas. The autoclaves were closed to the atmosphere during the introduction of the H₂S which was produced in a Kipp's type apparatus by the reaction:

$$Na_2S + 2HCl = 2NaCl + H_2S . (1)$$

The H_2S gas was purified by passing it through two gas-washing bottles filled with Milli-Q water (to remove HCl and SO_x gases) and then through a series of four cold traps (to remove condensable gases such as water vapour). As HCl has been shown to enhance the transport of gold in the gas phase (Archibald et al., 2001) and was one of the reagents used to produce H_2S , an aliquot of liquid from the second washing bottle was analyzed for its chloride content by HPLC (Activation Laboratories Ltd.). The concentration of this element was below the detection limit of the instrument (0.03 mg/L), and given that HCl partitions very strongly into the liquid phase, would have been even lower in the gas phase (NaCl was ignored as a possible contaminant because of its extremely low volatility). The cold traps cooled the H₂S to a temperature of -50 °C (using a mixture of dry CO₂ and methanol) and served to remove any H₂O introduced during washing (at this temperature the partial pressure of H₂O is ~10⁻⁵ bar) plus any condensable gases. Incondensable gases that might have remained after cleaning (e.g. HCl, which has a condensation temperature of -85 °C) would have been removed in the flow of gas exiting the autoclaves during the condensation of H₂S. The purity of H₂S produced and cleaned in the manner described above is considered to be ≥99.8 % by weight based on analyses reported in Migdisov et al. (1998).

A wire of native gold (Alfa Aesar, 99.95% purity) contained in a silica-glass holder was placed in each autoclave. In order to control the redox potential of the system, approximately 100 mg of powdered elemental sulphur (Alfa Aesar, 99.5% purity), which was sufficient to maintain equilibrium between H_2S gas and liquid sulphur at the conditions of the experiment according to reaction:

$$H_2S(g) = S(l) + H_2(g),$$
 (2)

was introduced into each autoclave in a separate open silica-glass holder. The holders were open at the top, and stood well above the liquid H_2S , thereby isolating the gold wire and native sulphur from the latter.

Experiments were performed at temperatures between 300 and 400 °C in an electric oven (Fisher Isotemp[®] models 818F and 550-126) equipped with an aluminum box (with a volume of about 0.05 m^3 , the walls are about 1 cm thick), in which the

autoclaves were placed, to reduce the temperature gradient. The choice of this range of temperatures was governed by the detection limit of the analytical method employed for gold analysis (at temperatures below 300 °C, the solubility of gold was expected to be too low to be measurable using instrumental neutron activation analysis, see below) and the critical temperature of sulphur (444.6 °C; Mills, 1974). The vertical temperature gradient, measured with two chromel-alumel thermocouples located at the top and bottom of the aluminum box, was generally less than 0.5 °C/m. A thermal regulator allowed the temperature to be controlled to an accuracy of ± 1 °C. At the conditions of the experiments, the liquid H₂S was converted entirely to gas (the critical point of H₂S is at 100 °C and 89 bar), which filled the autoclaves and reacted with the solids in the silicaglass holders (Fig. 2.1). At the end of a set of experiments, the autoclaves were quenched to room temperature in a water bath and further cooled to a temperature of \sim -75 °C in order to condense H₂S gas into liquid. The latter cooling ensured that, as was the case at the beginning of an experiment, gold wire and H₂S liquid were also spatially separated at the end of an experiment. The silica-glass holders containing sulphur and gold were then removed from the autoclaves and all the H₂S gas condensed into the liquid was released by slow boiling upon warming up the autoclave to room temperature. Sulphur-bearing holders were then weighed to determine the mass losses. Native sulphur and gold precipitated on the walls of the autoclaves during quenching were removed by washing with 1.5 to 3 mL of dilute (~10 wt. %) nitric acid at a temperature of 200 °C and subsequently with 2 to 4 mL of aqua regia at room temperature (HNO₃ and HCl of Fisher Scientific Optima[™] grade). The autoclaves were closed when heated in order to oxidize



Figure 2.1. Sketch of the experimental set-up. (a) Before an experiment, liquid H₂S gas is condensed in the autoclave at ~ -75 °C and gold wire and sulphur powder are placed in silica-glass holders arranged in the autoclave so that the solids are not in contact with liquid H₂S. (b) As the autoclave is heated to the target temperature of the experiment (300 to 400 °C), H₂S converts to gas, which reacts with the solids in the holders.

any native sulphur and other forms of reduced sulphur (e.g., polysulphanes, if present) that might have condensed on the walls and thereby ensure their complete dissolution in the washing solution (as sulphate). Washing of the walls of the autoclave was facilitated using a custom-designed rotating carousel that ensured semi-continuous contact of all the inner surfaces of the autoclave with the washing solution. The concentration of gold in the washing solutions, and hence dissolved in H₂S, was determined using instrumental neutron activation analysis (INAA) at Ecole Polytechnique (University of Montreal). The detection limit of the analytical technique was 0.1 ppb (1 ppb = 1 μ g/L) and the precision was $\pm 5\%$ for samples with concentrations greater than 1 ppb and ± 0.05 ppb for samples containing lower concentrations of Au. In order to ensure that no gold remained in the autoclaves after the first washing, the washing procedure was repeated and the resulting solutions also analyzed using INAA. The concentration of gold in these second-washing solutions was consistently below the detection limit, indicating that no gold was missed during the initial washing. The amount of sulphur transferred to the gas phase from the silica glass holder during an experiment was determined to an accuracy of ± 0.1 mg by weighing the holders loaded with sulphur before and after each run.

A series of blank experiments (three experiments at each temperature investigated) was conducted in an atmosphere free of hydrogen sulphide (i.e., nitrogen gas). The concentration of Au determined for these was below the detection limit of the analytical technique (0.1 ppb) indicating that there was no significant transport and precipitation of gold due solely to volatilization and condensation of the metallic gas.

The attainment of equilibrium was tested by means of a set of kinetic experiments of varying duration (from 1 to 22 days) at the lowest temperature investigated (300 °C).

As the pressures in the autoclaves varied slightly (± 10 bar) because of the difficulty in controlling the amount of H₂S condensed, it was, however, necessary to correct Au fugacities (their calculation is discussed below) to an arbitrarily chosen H₂S fugacity of 100 bar for purposes of comparison, (this was done using the dependencies of Au fugacity on the fugacity of H₂S gas determined from later experiments). The results of these time-series experiments are presented in Figure 2.2 and show that reproducible (within 5%) Au fugacities were obtained in less than 10 days. Subsequent experiments were run for longer duration (>12 days), thereby ensuring that the measured metal concentrations closely approached the equilibrium concentrations.

2.4. RESULTS

The experiments were performed at temperatures of 300, 350 and 400 °C, and pressures varying from 25 to 230 bar. Owing to the very low vapour pressure of sulphur species in the experiment (typically less than 1 bar) and vanishingly small vapour pressure of gold ($<10^{-5}$ bar) compared to that of H₂S, the total pressure of the system was assumed to be equal to that of pure hydrogen sulphide. Pressure and fugacity coefficients were calculated using the accurately determined autoclave volume (minus the volume of the holders with gold wire and elemental sulphur), the mass of H₂S introduced and the equation of state for hydrogen sulphide gas (Rau and Mathia, 1982).

Assuming ideal behaviour of volatile metal compounds, the fugacity of the goldbearing compound was calculated using the ideal gas law, $f \cong P = NRT/V$, where P is the



Figure 2.2. Results of kinetic experiments at 300 °C and pressure normalized to 100 bar. Concentrations of the dissolved Au presented as $log f_{"Au(g)"}$ were corrected to an arbitrarily chosen H₂S fugacity of 100 bar because of the difficulty in maintaining the same pressure conditions for a full set of time-series runs (the pressure in each autoclave was slightly different due to small differences in the amount of H₂S introduced into them). After 10 days, the system attained a plateau concentration interpreted to represent equilibrium. Comparison of the results of these and subsequent experiments suggests that the equilibrium concentration is reproducible to ±5% (see text for further explanation).

H_2S	V	Р	φ_{H_2S}	$log f_{H_2S}$	<i>"Au(g)"</i> ¹	$\log f_{"Au(g)"}^{2}$	Au ³	
mole	cm ³	bar		bar	x10 ¹¹ mole	experimental	ppb	
300 °C								
0.041	37.7	49.0	0.95	1.67	0.36	-8.35	0.50	
0.047	37.6	56.4	0.94	1.73	0.89	-7.95	1.1	
0.048	37.5	57.7	0.94	1.74	0.71	-8.04	0.85	
0.075	38.5	85.1	0.92	1.89	0.71	-8.06	0.55	
0.073	36.8	86.3	0.92	1.90	0.71	-8.04	0.56	
0.085	37.4	98.0	0.91	1.95	0.71	-8.04	0.48	
0.088	37.5	101	0.90	1.96	0.53	-8.17	0.35	
0.089	37.2	103	0.90	1.97	1.4	-7.74	0.92	
0.109	38.2	120	0.89	2.03	2.1	-7.58	1.1	
0.137	36.82	153	0.86	2.12	3.2	-7.38	1.3	
0.159	37.7	171	0.85	2.16	2.3	-7.54	0.84	
0.207	37.6	215	0.82	2.25	3.4	-7.37	0.94	
350 °C								
0.020	37.1	26.9	0.98	1.42	0.36	-8.30	1.0	
0.023	37.2	31.2	0.98	1.48	0.71	-8.01	1.8	
0.043	37.0	57.3	0.96	1.74	0.71	-8.00	0.96	
0.052	36.7	70.3	0.95	1.82	1.6	-7.65	1.8	
0.066	36.7	87.4	0.94	1.91	1.6	-7.65	1.4	
0.104	36.7	133	0.91	2.08	4.6	-7.19	2.6	

Table 2.1. The solubility of gold in H_2S gas.

H_2S	V	Р	φ_{H_2S}	$log f_{H_2S}$	"Au(g)" ¹	$\log f_{"Au(g)"}^{2}$	Au ³
mole	cm ³	bar		bar	x10 ¹¹ mole	experimental	ppb
0.140	36.9	174	0.88	2.19	4.3	-7.22	1.8
0.146	37.0	181	0.88	2.20	20	-6.55	8.0
0.188	37.2	228	0.86	2.29	5.3	-7.13	1.6
400 °C							
0.024	37.0	35.3	0.98	1.54	3.6	-7.27	8.6
0.024	36.9	35.4	0.98	1.54	5.0	-7.12	12
0.030	36.6	44.9	0.98	1.64	10	-6.80	20
0.045	37.2	65.1	0.96	1.80	45	-6.17	58
0.067	53.8	66.9	0.96	1.81	23	-6.62	20
0.063	38.5	87.9	0.95	1.92	104	-5.82	95
0.093	53.4	92.4	0.95	1.94	57	-6.22	36
0.128	54.3	126	0.94	2.07	82	-6.07	37
0.102	38.0	140	0.93	2.12	90	-5.88	51
0.152	53.4	148	0.93	2.14	83	-6.06	32
0.112	38.1	153	0.92	2.15	100	-5.84	51
0.118	38.3	159	0.92	2.17	122	-5.75	60
0.150	38.5	199	0.90	2.26	60	-6.06	23

Table 2.1. (continued)

V-volume, P-pressure, φ_{H_2S} -fugacity coefficient

1 - amount of Au transported from the gold wire to the gas phase during the experiment

2 - calculated from the experimental data using ideal gas law (see text for explanation)

3 – the solubility of Au in H_2S gas in the experiments presented as ppb = μ g/kg

partial pressure of the gaseous Au complex, V is the volume of the autoclave, N the number of moles of Au dissolved in the gas phase (which was calculated from the concentration of Au measured in washing solutions and therefore represents the amount of Au transported from the gold wire to the gas phase), R the gas constant and T the temperature of the experiment. The results of the experiments are reported in Table 2.1 as logarithms of the fugacity of the gold-bearing gas species, $log f_{"Au(g)"}$, and concentrations of gold dissolved in H₂S (ppb, i.e., µg per kg of H₂S). The solubility of Au in H₂S gas was found to range from 0.4 to 1.4 ppb at 300 °C, 1 to 8 ppb at 350 °C and 8.6 to 95 ppb at 400 °C (Fig. 2.3) and a positive correlation of $log f_{"Au(g)"}$ to $log f_{H_2S(g)}$ was observed at all temperatures investigated (see Fig. 2.7 and discussion below).

2.5. DISCUSSION

2.5.1. The Solubility of Au in H₂S gas

Thermochemical properties of the following gaseous species of gold, Au, AuH and AuS, are reported in Mills (1974) and Barin et al. (1977). Evidence for the existence of the molecule Au₂S(g) by mass spectrometry was reported by Smoes and Drowart (1968), but no information was provided on its stability, and it is not considered in our calculations. Calculations based on the available thermodynamic data show that, among these species, only AuS(g) is likely to play a significant role in the vapour transport of gold (Symonds and Reed, 1993; Taran et al., 2000). We therefore initially attempted to describe the



Figure 2.3. A plot of the concentration of Au (in ppb or $\mu g/kg$) dissolved in H₂S gas versus pressure at the conditions of the solubility experiments (temperatures of 300, 350 and 400 °C and pressures of 25 to 230 bar).

solubility of gold in H₂S gas solely in terms of this species and an assumption that there are no interactions between the solvent (H₂S gas) and AuS(g), i.e., that the behaviour of the latter is ideal. The experimental system was assumed to contain the following compounds: native gold, Au(g), AuS(g), S(l), S_i(g), H₂S(g), H₂S(l), H₂S_j(g), and H₂S_k(l), where *i* (representing gaseous sulphur polymers) varies from 1 to 8 (Rau et al., 1973), *j* (representing gaseous hydrogen polysulphanes) varies from 2 to 6 (Féher and Winkhaus, 1957; Migdisov et al., 1998), and *k* (representing liquid polysulphanes) is greater than 1 (Steudel, 2003). A variety of gaseous and liquid hydrogen polysulphanes are likely to have formed as a result of the interaction of sulphur with H₂S and, as will be shown below, influence the mass balance of sulphur in the system (Migdisov et al., 1998; Steudel, 2003) as well as complicate the final gold fugacity calculations.

The solubility of gold in the vapour phase was described initially by the following reaction:

$$Au(s) + H_2S(g) = AuS(g) + H_2(g)$$
 (3)

This reaction is dependent on $f_{H_2(g)}$. However, when combined with the reaction

$$H_2(g) + S(l) = H_2S(g),$$
 (4)

it yields the reaction

$$Au(s) + S(l) = AuS(g), \tag{5}$$

which depends instead on the activity of liquid sulphur. In order to quantitatively estimate the equilibrium constant for reaction 3 or 5, and hence, to obtain values of the solubility of Au in H_2S gas, it is essential to know either the fugacity of hydrogen gas or the activity of liquid sulphur at equilibrium (both effectively represent the same redox equilibria). Owing to the difficulty in determining $f_{H_2(g)}$ at the experimental conditions, it was necessary to evaluate the solubility of Au in H₂S gas using the activity of liquid sulphur and reaction 5.

2.5.2. Activity of Liquid Sulphur in the System S-H₂S

Owing to the appreciable consumption of H_2S gas that occurs during its interaction with molten sulphur (Fanelli, 1949), the activity of liquid sulphur cannot be assumed to be equal to unity. Moreover, evaluation of this activity is complicated by the fact that the consumption of H_2S , as first suggested by Fanelli (1949) and subsequently demonstrated by Wiewiorowski and Touro, (1966), is due not only to simple dissolution of H_2S but also to the formation of liquid polysulphanes (H_2S_k), via the reaction:

$$H_2S(g) + (k-1)S(l) = H_2S_k(l)$$
(6).

Wiewiorowski and Touro, (1966) showed, furthermore, that the solubility of H_2S gas in molten sulphur actually decreases with increasing temperature and that at temperatures above about 150 °C, formation of polysulphanes predominates over simple dissolution of H_2S (Fig. 2.4). The dissolution of H_2S gas into the sulphur melt and the formation of polysulphane species result in a decrease in the mole fraction, and hence activity, of liquid sulphur.

Inasmuch as the only experimental data available on the stability of liquid polysulfanes in the melt are for temperatures below 180 °C (Wiewiorowski and Touro, 1966), neither the values for the mole fraction of liquid sulphur in the melt nor the corresponding activity coefficients are known at the temperatures considered in our



Figure 2.4. The solubility of hydrogen sulphide gas in liquid sulphur. The data are from the solubility experiments of Fanelli (1949; – closed circles) and Wiewiorowski and Touro (1966; – open circles). The net contributions of the species H_2S and H_2S_k to the total solubility of hydrogen sulphide (H_2S^{total}) in sulphur melt were measured using direct infrared spectroscopy by Wiewiorowski and Touro (1966) and are shown by the black and grey dashed lines, respectively.

experiments (300-400 °C). On the other hand, the volatility of sulphur species and thus the amount of sulphur that can be transported in the gas phase are related to the activity of liquid sulphur through the following reactions:

$$iS(l) = S_{i}(g), \ K_{7} = \frac{f_{S_{i}(g)}}{a_{S(l)}^{i}}$$
(7)

and

$$H_2S(g) + (j-1)S(l) = H_2S_j(g), \ K_8 = \frac{f_{H_2S_j(g)}}{f_{H_2S(g)} \cdot a_{S(l)}^{j-1}}$$
(8)

As the equilibrium constants for these reactions can be calculated from thermodynamic data (Mills, 1974; Suleimenov and Ha, 1998), it is thus possible to use them to extract values of the activity of S(l) in the melt by determining the amount of sulphur transported into the gas phase coexisting with the melt. However, given that there are no data on the fugacity coefficients of the different sulphur species in the gas phase, it is necessary to assume that they are equal to their corresponding partial pressures and thus that:

$$P_{S_i(g)} \cong f_{S_i(g)} = K_7 \cdot a_{S(l)}^i \tag{9}$$

and

$$P_{H_2S_j(g)} \cong f_{H_2S_j(g)} = K_8 \cdot f_{H_2S(g)} \cdot a_{S(l)}^{j-1} \qquad . \tag{10}$$

The mass of sulphur transported into the gas phase was therefore calculated from the ideal gas law $(N_S = \frac{P_{S(g)}^{total}V}{RT})$, where N_S is the number of moles of sulphur lost from the holder during the experiment, V is the effective volume of the autoclave, R the gas constant and T the temperature of the experiment). The activity of liquid sulphur was in turn determined using the relationship:

$$N_{S} = \left(\sum_{i=1}^{8} i \cdot K_{S_{i}} \cdot a_{S(l)}^{i} + \sum_{j=2}^{6} K_{H_{2}S_{j}} \cdot f_{H_{2}S(g)} \cdot a_{S(l)}^{j-l}\right) \cdot \frac{V}{RT}$$
(11)

The values of K_{S_i} and $K_{H_2S_j}$ were calculated from Mills (1974) and Suleimenov and Ha (1998), respectively, the value for $f_{H_2S(g)}$ was evaluated from the equation of state for H₂S (Rau and Mathia, 1982), *V* is the known volume of the autoclave, *T* is the temperature of the experiment and N_S is the mass loss of sulphur determined experimentally. Equation 11 thus has only one unknown, namely the activity of liquid sulphur, $a_{S(l)}$, and could therefore be solved for this parameter. It should be noted, however, that as the activity coefficient of liquid sulphur in the melt is unknown, this solution did not provide any information on the mole fraction of sulphur in the melt or further constrain the composition of the latter.

Values of the activity of liquid sulphur were calculated from a polynomial equation fitted to the experimental data at 300, 350 and 400 °C (Table 2.2). The uncertainty on the activity of sulphur calculated from the experimental data (propagated from the errors related to experimental measurements) is less than 0.01; thus statistical standard deviation of the fit (Table 2.2) should be used further to account for the error associated with calculations of the activity of molten sulphur at the conditions of interest.

From Figure 2.5 it is evident that the activity of liquid sulphur in the melt decreases with increasing $f_{H_2S(g)}$ due to the dissolution of H₂S gas and the resultant formation of liquid polysulphanes. However, the extent to which $a_{S(l)}$ decreases depends on temperature. For example, between 300 and 350 °C, $a_{S(l)}$ decreases to 0.47, whereas at 400 °C it only decreases to 0.7 (Fig. 2.5), which is consistent with the observation of

Table 2.2. Coefficients for the polynomial equation employed to estimate the activity of liquid sulphur $(a_{S(l)})$.

T °C	$a_{S(l)} = \mathbf{a} + \mathbf{b} \cdot f_{H_2S(g)} + \mathbf{c} \cdot f_{H_2S(g)}^2 + \mathbf{d} \cdot f_{H_2S(g)}^3$						
	а	b	с	d	σ		
300	0.8980	-7.49·10 ⁻³	3.37.10-5		±0.07		
350	1.0108	$-4.67 \cdot 10^{-3}$	-6.47·10 ⁻⁶	9.15·10 ⁻⁸	±0.02		
400	1.0041	-1.16.10-4	- 2.07·10 ⁻⁵	6.82·10 ⁻⁸	±0.01		

 σ represents the statistical standard deviation of the fit



Figure 2.5. The activity of S in molten sulphur as a function of the fugacity of H_2S in the system. A polynomial equation (Table 2.2) fitted to the experimental data at 300, 350 and 400 °C (with 1 σ standard deviations of ±0.07, ±0.02 and ±0.01, respectively) was used to calculate the activity of molten sulphur at the conditions of interest (see text for further explanation).

Fanelli (1949) that the total solubility of H_2S in molten sulphur reaches a broad maximum (plateau value) between 300 and 370 °C (Fig 2.4). Another pertinent observation is that the cumulative partial pressure of gaseous hydrogen polysulphanes exceeds that of gaseous elemental sulphur species at fugacities of H_2S gas above about 20 bar (Fig. 2.6), which agrees well with the findings of Migdisov et al. (1998), who showed that the solubility of sulphur in H_2S gas at temperatures above 200 °C can be attributed entirely to the formation of gaseous hydrogen polysulphanes.

2.5.3. The Solubility of Au as AuS(g)

Having determined the activity of liquid sulphur, the fugacity of AuS(g) was calculated from the expression for reaction 5, the equilibrium constant of which is given by:

$$\log K_{5} = \log f_{AuS(g)} - \log a_{S(l)} - \int_{P_{l}}^{P_{2}} \frac{V^{\circ}}{RT} dp .$$
(12)

The equilibrium constant, K_5 , was calculated from standard thermodynamic data (Mills, 1974), the activity of liquid sulphur $a_{S(l)}$ was obtained from Table 2.2, V° is the sum of the molar volumes of native gold and sulphur, and R is the gas constant. The last term of the equation is the Poynting pressure correction (Sandler, 1989). However, over the range of conditions at which the experiments were conducted, corrections provided by this term do not exceed 0.05, which is much lower than the experimental error, and therefore can be ignored. The values of gold solubility in H₂S gas calculated using equation 12 are presented in Table 2.3 (as $log f_{"Au(g)"}$) and illustrated in Figure 2.7.



Figure 2.6. The sum of the partial pressures of gaseous sulphur species (S_i and H_2S_j) as a function of the fugacity of H_2S gas. Circles represent the cumulative partial pressure of sulphur species determined in the experiments. The partial pressures of gaseous polysulphanes (dashed line) and sulphur polymers (dashed-dotted line) were calculated from the thermodynamic data taking into account the variable activity of sulphur with respect to the fugacity of H_2S gas (see text for details). At a pressure above about 20 bar, hydrogen polysulphanes replace sulphur polymers as the dominant sulphur species in H_2S gas and at pressures above 70 bar are the principal form of dissolved sulphur in the gas phase.
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Table 2.3. Calculated fugacities of gaseous gold species based on experimental data reported in this study compared with values calculated from published thermodynamic data. (The activity of sulphur $a_{S(l)}$ was calculated from the polynomial equations given in Table 2.2.)

P bar	$log f_{H_2S(g)}$ bar	a _{S(l)}	$\log f_{"Au(g)"}^{1}$ calculated as AuS(g)	$log f_{"Au(g)"}^{2}$ experimental	$\log f_{"Au(g)"}^{3}$ modeled as $AuS \cdot (H_2S)_n$	
			300 °C			
49.0	1.67	0.63	-11.62	-8.35	-8.35	
56.4	1.73	0.60	-11.65	-7.95	-8.26	
57.7	1.74	0.60	-11.65	-8.04	-8.25	
85.1	1.89	0.52	-11.71	-8.06	-8.00	
86.3	1.90	0.52	-11.72	-8.04	-8.00	
98.0	1.95	0.50	-11.73	-8.04	-7.92	
101	1.96	0.49	-11.74	-8.17	-7.90	
103	1.97	0.49	-11.74	-7.74	-7.89	
120	2.03	0.47	-11.76	-7.58	-7.78	
153	2.12	0.49	-11.75	-7.38	-7.62	
171	2.16	0.52	-11.74	-7.54	-7.54	
215	2.25	0.66	-11.67	-7.37	-7.34	
350 °C						
26.9	1.42	0.88	-9.83	-8.30	-8.30	
31.2	1.48	0.86	-9.84	-8.01	-8.21	
57.3	1.74	0.75	-9.89	-8.00	-7.84	
70.3	1.82	0.70	-9.92	-7.65	-7.72	
87.4	1.91	0.64	-9.96	-7.65	-7.60	
133	2.08	0.51	-10.04	-7.19	-7.38	
174	2.19	0.47	-10.07	-7.22	-7.22	
181	2.20	0.47	-10.07	-6.55	-7.20	
228	2.29	0.53	-10.01	-7.13	-7.03	

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Р	$log f_{HS(a)}$		$\log f_{"Au(g)"}$	$\log f_{"Au(g)"}^2$	$\log f_{"Au(g)"}^{3}$
bar	bar	u S(l)	calculated	experimental	modeled
			as AuS(g)		as $AuS \cdot (H_2S)_n$
			400 °C		
35.3	1.54	0.98	-8.42	-7.27	-7.13
35.4	1.54	0.98	-8.42	-7.12	-7.12
44.9	1.64	0.96	-8.43	-6.80	-6.91
65.1	1.80	0.93	-8.44	-6.17	-6.57
66.9	1.81	0.93	-8.44	-6.62	-6.55
87.9	1.92	0.89	-8.45	-5.82	-6.31
92.4	1.94	0.88	-8.46	-6.22	-6.26
126	2.06	0.82	-8.48	-6.07	-6.01
140	2.12	0.79	-8.50	-5.88	-5.91
148	2.14	0.77	-8.50	-6.06	-5.86
153	2.15	0.77	-8.51	-5.84	-5.84
159	2.17	0.76	-8.51	-5.75	-5.80
199	2.26	0.71	-8.53	-6.06	-5.62

Table 2.3. (continued)

1 – calculated from thermodynamic data using reaction 5: Au(s) + S(l) = AuS(g)

2 - calculated from experimental data

3 – modeled from experimental data for reaction 15: $Au(s) + nH_2S(g) + S(l) = AuS \cdot (H_2S)_n(g)$

Figure 2.7. A plot of $log f_{"Au(g)"}$ versus $log f_{H_2S(g)}$ comparing the experimentally determined fugacity of dissolved gold to that predicted assuming that this fugacity is dependent entirely on the formation of gaseous gold sulphide AuS(g) (dashed line). The calculated values are 10³ to 10⁴ lower at 300 °C (a), 10^{1.5} to 10³ lower at 350 °C (b) and 10 to 10³ lower at 400 °C (c). Unlike the experimental data, the calculated fugacity of gaseous gold species does not correlate positively with the fugacity of H₂S gas (solid lines reflect the positive trend of the dependence of $log f_{"Au(g)"}$ on $log f_{H_2S(g)}$; see text for further explanation).



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As is evident from Figure 2.7, there are significant discrepancies between the calculated values of $log f_{"Au(g)"}$ and those determined experimentally. The calculated values are 10³ to 10⁴ lower at 300 °C, 10^{1.5} to 10³ lower at 350 °C and 10 to 10³ lower at 400 °C. Furthermore, unlike the experimental data, the calculated fugacity of gaseous gold species does not correlate positively with the fugacity of H₂S gas. These observations indicate clearly that the formation of gaseous AuS cannot alone be responsible for the solubility of gold in H₂S gas.

2.5.4. Au Dissolution as a Solvated Species

The positive dependence of the dissolved gold concentration on the fugacity of H₂S gas suggests that gold solubility may be controlled in part by a solvated species resulting from solute-solvent interaction. By analogy with models developed for solid-H₂O (vapour) systems (Migdisov et al., 1999; Archibald et al., 2001 and 2002; Migdisov and Williams-Jones, 2005; Rempel et al., 2006), we propose that this species has the form of an uncharged solvated gaseous complex with reduced sulphur, e.g., $AuS \cdot (H_2S)_n$ or $AuHS \cdot (H_2S)_n$, resulting from reactions of the type:

$$Au(s) + (n+1)H_2S(g) = AuS \cdot (H_2S)_n(g) + H_2(g),$$
(13)

$$Au(s) + (n+1)H_2S(g) = AuHS \cdot (H_2S)_n(g) + 0.5H_2(g);$$
(14)

where *n* is the solvation number of the gold species or the number of H_2S molecules in a shell immediately adjacent to a gold-bearing species held there by van der Waals bonding

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(akin to a hydration shell). Even though this number represents a statistical approximation and is dependent on both temperature and pressure, we still can consider reactions 13 and 14 as being stoichiometric based on the fairly good assumption that, within the experimental range of pressures, the solvation number is pressure-independent. This allows us to calculate the solvation number and the equilibrium constant for the solubility reaction in the manner described by Migdisov et al. (1999).

Unfortunately, we cannot distinguish between the above species based on the experimental data reported earlier. Nevertheless, as AuS(g) is the most stable known gold species in the Au-H-S gas system, it is reasonable to propose that the gaseous volatile complex responsible for the high solubility of gold in H₂S gas has the form $AuS \cdot (H_2S)_n$. It is equally possible, given the importance of $AuHS^\circ$ species in aqueous liquids (e.g., Stefansson and Seward, 2004), that the species controlling gold solubility in H₂S gas has the form $AuHS \cdot (H_2S)_n$. In the following paragraphs, we evaluate formation constants for these two species.

As discussed above, hydrogen fugacity is related to the activity of liquid sulphur and fugacity of H_2S gas in the system through reaction 4. Therefore, by combining reactions 4 and 13 and reactions 4 and 14 we obtain the following reactions describing equilibrium in the system:

$$Au(s) + nH_2S(g) + S(l) = AuS \cdot (H_2S)_n(g),$$
 (15)

$$Au(s) + (n+0.5)H_2S(g) + 0.5S(l) = AuHS \cdot (H_2S)_n(g).$$
(16)

The equations for the equilibrium constants of these reactions are:

$$\log K_{15} = \log f_{AuS \cdot (H_2S)_n(g)} - \log a_{S(l)} - n \cdot \log f_{H_2S(g)},$$
(17)

$$\log K_{16} = \log f_{AuHS\cdot(H_2S)_n(g)} - 0.5 \cdot \log a_{S(l)} - (n+0.5) \cdot \log f_{H_2S(g)},$$
(18)

respectively.

The procedure used to determine the solvation number of the gaseous complex was similar to that employed in previous investigations of metal transport by vapour (Migdisov et al., 1999; Archibald et al., 2001 and 2002; Zakaznova-Iakovleva et al., 2001; Migdisov and Williams-Jones, 2005; Rempel et al., 2006). However, unlike the dependencies of log $f_{"Me(g)"}$ on log $f_{gas-solvent}$, which were linear in these studies, the dependency in the present case is nonlinear due to the variable activity of liquid sulphur. The solvation number *n* and equilibrium constant for reactions 15 and 16 were calculated iteratively using MATLAB[®] software from initial guesses and progressive minimization of the function *U*:

$$U = \sqrt{\sum \left(\frac{f^{exp} - f^{model}}{f^{model}}\right)^2} \quad , \tag{19}$$

where f^{exp} is the fugacity of the gold-bearing gaseous complex calculated from experimental data using assumptions discussed above, f^{model} is the modeled fugacity of the corresponding gaseous complex $(AuS \cdot (H_2S)_n \text{ or } AuHS \cdot (H_2S)_n)$ at each fugacity of H_2S investigated. The term f^{model} was evaluated using the solvation number and the equilibrium constant for the corresponding complexation reaction (i.e., for the formation of $AuS \cdot (H_2S)_n$ or $AuHS \cdot (H_2S)_n$), which were used as adjustable parameters in the iteration procedure. The algorithm employed in the minimization was the Nelder-Mead simplex search described by Nelder and Mead (1965), and Dennis and Woods (1987).

The equilibrium constant for the reaction describing the formation of the gaseous goldbearing complex increases with increasing temperature from 300 to 400 °C (Table 2.4). The propagated errors on the calculated values of the logarithm of the equilibrium constants are up to 0.07, 0.03 and 0.02 at temperatures of 300, 350 and 400 °C, respectively. The values of the standard deviation of the fit are significantly greater (about 0.2-0.3), and therefore are listed in Table 2.4 as the calculated uncertainties. The solvation number (referred to below as n_{15} and n_{16} in reactions 15 and 16, respectively), however, is higher at 400 °C ($n_{15} = 2.2$, $n_{16} = 1.7$), than at 300 and 350 °C ($n_{15} = 1.8$ and 1.7 and $n_{16} =$ 1.2 and 1, respectively), which is unusual for gaseous metallic species. In contrast to metallic species in H₂O and H₂O-HCl gases (Williams-Jones et al., 2002 and references therein; Migdisov and Williams-Jones, 2005; Rempel et al., 2006), the dependence of the fugacity of the gaseous gold complex on the total fugacity of H_2S gas (Table 2.3) is slightly nonlinear due to the effect of the change in the activity of liquid sulphur with $f_{H_2S(g)}$ (Fig. 2.8). This deviation from nonlinearity is more pronounced at temperatures of 300 and 350 °C than at 400 °C due to the much lower plateau values of $a_{S(l)}$ with increasing $f_{H_2S(g)}$ (see Fig. 2.5).

2.5.5. Comparison to Previous Studies

The only previous study to investigate the solubility of metals in H₂S gas is that of Zakaznova-Iakovleva et al. (2001). Using an approach similar to that described in our study, the authors concluded that the solubility of stibnite (Sb_2S_3) in H₂S gas is due to the formation of the solvated gaseous complex $Sb_2S_3 \cdot (H_2S)$. Comparing the solubility

Table 2.4. Values of the solvation number, *n*, log K_{15} and log K_{16} for the reactions $Au(s) + nH_2S(g) + S(l) = AuS \cdot (H_2S)_n(g)$ and

$$Au(s) + (n + 0.5)H_2S(g) + 0.5S(l) = AuHS \cdot (H_2S)_n(g)$$

	$AuS \cdot (H_2S)_n(g)$		$AuHS \cdot (H_2S)_n(g)$	
T°C −	<i>n</i> ₁₅	$\log K_{15}$	<i>n</i> ₁₆	$\log K_{16}$
300	1.8	-11.1±0.2*	1.2	-11.1±0.2
350	1.7	-10.7±0.3	1.0	-10.5±0.3
400	2.2	-10.6±0.2	1.7	-10.4±0.2

calculated using the minimization function given by equation 19.

* The uncertainty represents the standard deviation for the experimental data $(\pm 1\sigma)$.



Figure 2.8. A plot of the experimentally determined solubility of Au in H₂S gas at temperatures of 300 °C (a), 350 °C (b) and 400 °C (c). The solid lines represent the values calculated in this study for the solubility of the gaseous species, $AuS \cdot (H_2S)_n$ or $AuHS \cdot (H_2S)_n$ (*n* varying from 1 to 2.2 at temperatures between 300 and 400 °C, see text for details). The nonlinear dependence of the calculated solubility of Au in H₂S gas is due to the deviation of $a_{S(l)}$ from unity.

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isotherms presented in that study with those obtained in our study, it is clear that, despite the substantially greater solubility of stibnite, their form is essentially the same, reflecting a very similar process of solvation of metal-bearing species by H₂S gas molecules (Fig. 2.9).

Although direct comparison of the results of this study to those obtained previously for H₂O-HCl mixtures (Archibald et al., 2001) is difficult, it is worth noting that the solubility of Au in H₂S gas is about one to two orders of magnitude greater than that obtained for Au in the system H₂O-HCl at similar conditions (Fig. 2.10). It is also worth noting that gold solubility in the H₂O-HCl system is retrograde at temperatures above 300 °C, whereas the stability of gold species in H₂S increases appreciably with temperature over the range of temperatures investigated (300 to 400 °C). However, the solvation number of gold chloride species dissolved in H₂O-HCl gas mixtures is greater (n = 3 to 5) than for species dissolved in H₂S gas (n = 1 to 2). Consequently, the solubility of gold as a chloride complex in natural chloride-bearing vapours will increase more rapidly with pressure than in an H₂S-bearing system. On the other hand, the gold solvation number of $AuCl \cdot (H_2O)_n$ decreases with decreasing temperature between 360 and 300 °C, whereas that of $AuS \cdot (H_2S)_n$ or $AuHS \cdot (H_2S)_n$ remains constant.

2.5.6. The Capacity of Natural H₂S-bearing Vapour to Transport Gold

In order to evaluate the possible effect of H_2S complexation and solvation on the transport of gold in the vapour phase, we calculated the likely concentration of gold in a hypothetical hydrothermal vapour. We assumed that the vapour phase is produced by



Figure 2.9. A comparison of the solubility of gold in H₂S gas determined in this study (as $AuS \cdot (H_2S)_n$ or $AuHS \cdot (H_2S)_n$ with n = 1 to 2.2 at T = 300 to 400 °C) with the solubility of stibuite (Sb₂S₃) in H₂S (as $Sb_2S_3 \cdot (H_2S)$ at T = 300 to 360 °C) measured by Zakaznova-Iakovleva et al. (2001).



Figure 2.10. A comparison of the solubility of gold in H₂O-HCl vapour mixtures (at f_{HCl} = 0.065 bar) measured by Archibald et al. (2001) with that in H₂S gas determined in this study. The solubility of Au in H₂O-HCl vapour mixtures is controlled by the formation of a hydrated gold chloride complex $AuCl \cdot (H_2O)_n$ with n = 3 to 5, and that in H₂S gas by the formation of the solvated hydrosulphide complexes $AuS \cdot (H_2S)_n$ or $AuHS \cdot (H_2S)_n$ with n = 1 to 2.2.

open system boiling, at a temperature of 400 °C, of a fluid analogous to that exsolved from a felsic calc-alkaline magma. The fluid has a salinity of 2 m NaCl, which is similar to that exsolved from the magma in Bingham porphyry (e.g., Redmond et al., 2004) and predicted on theoretical grounds by Burnham (1979). The H₂S concentration was assumed to be 0.1 m, based on the composition of typical geothermal waters and a correction to account for the dependence of the latter on temperature (Barnes and Seward, 1997). The data of Suleimenov and Krupp (1994) for the system H₂O-H₂S-NaCl were used to establish the partitioning of H₂S between liquid and vapour at 400 °C. The solubility of gold was assumed to be controlled by reaction 15 (reaction 16 would have yielded an identical result) and redox conditions buffered by the pair H₂S/S (i.e., between those of the hematite-magnetite and quartz-fayalite-magnetite buffers); note that Au solubility increases with increasing f_{Q_1} (reaction 13).

Based on the above assumptions, we calculated that, after 0.1% boiling, the mole fraction of H_2S in the vapour was effectively 1 (the *PVTx* properties of the fluids were estimated from data for the NaCl-H₂O system reported by Sourirajan and Kennedy, 1962) and after 1% boiling had decreased to 0.18 (Fig. 2.11a). At these mole fractions of H_2S , the corresponding concentrations of gold are 90 and 2 ppb, respectively (Fig. 2.11b). For comparison, the time required to form a hydrothermal deposit containing 50 tons of gold (which is within the size range of numerous economic deposits) from a fluid with a concentration of 1 ppb Au is 43 Ka assuming a depositional efficiency of 50% and a discharge rate similar to that of modern geothermal systems (e.g., 75 kg/sec – Waiotapu; Henley, 1985). This is much less than the lifespan of many gold-depositing hydrothermal systems, e.g., the duration of the Far South-East-Lepanto system was about 300 ka



Figure 2.11. The calculated mole fraction of H_2S in the vapour phase (a) and the calculated solubility of Au in the vapour phase (b) as a function of the extent of boiling of a 2 m NaCl aqueous liquid at 400 °C initially containing 0.1 m H_2S .

(Arribas et al., 1995). Hence, our calculations show that it is possible for boiling to produce a vapour with the concentration of H_2S needed to economically transport significant quantities of gold but only if the proportion of vapour relative to that of the pre-boiled liquid is small.

2.6. CONCLUSIONS

The results of this experimental study support suggestions of other researchers that complexation with reduced sulphur may play an important role in the transport of gold in the vapour phase of hydrothermal systems. The solubility of Au in hydrogen sulphide gas can reach values of 1.4 ppb (wt.) at 300 °C, 8 ppb at 350 °C and 95 ppb at 400 °C, and we propose that this solubility is governed by the formation of a H₂S-solvated gaseous complex having the form $AuS \cdot (H_2S)_n$ or $AuHS \cdot (H_2S)_n$, where *n* is between 1 to 2 at temperatures ranging from 300 to 400 °C and pressures up to 230 bar. Although the experiments described here were not carried out at conditions directly applicable to nature, they do provide strong evidence that H₂S can play a major role in dissolving gold in hydrothermal vapours and that this role may be key to understanding the genesis of porphyry and epithermal gold deposits.

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INTRODUCTION TO CHAPTER 3

In the previous chapter, the stability and stoichiometry of gold was investigated in vapours in the system Au-H-S. It was shown experimentally that solvation of sulphide species of gold by pure H₂S gas significantly enhances the solubility of gold in the gas phase. Since solvation and low-energy interactions are involved in the stabilization of gold by H_2S gas, it is reasonable to assume that water molecules may also participate in this type of gas phase reaction, particularly as water and hydrogen sulphide molecules have similar polar configurations and both have a significant dipole moment. The logical next step is to conduct experiments of the type referred to above on vapours in the system Au-H-S-O. However, in order to conduct such experiments, it is necessary to know accurately the properties of H_2O-H_2S gas mixtures. Unfortunately, these properties have not been determined except at low temperature and pressure. Moreover, because of nonideal behaviour related to the polar nature of the molecules of water and hydrogen sulphide, as well as to possible association of molecules due to hydrogen bonding, these properties cannot be satisfactorily estimated using existing data and models. In order to proceed with gold speciation experiments in the system H-S-O, a study was undertaken of the properties of H₂O-H₂S mixtures.

The volumetric properties of H_2O-H_2S gas mixtures were determined experimentally for both single and two-phase fluid mixtures at temperatures up to 400 °C. Based on the experimental data, the properties were modelled using cubic equations of state and refined by adjusting with system-specific binary interaction parameters. Employing composition- or density-dependent mixing rules, the resulting equations allow accurate estimates of the properties of gas mixtures, and support a thermodynamic model describing the behaviour of the H_2O-H_2S fluids at the conditions of vapour-liquid equilibrium. The fugacity coefficients of components in the mixtures can be evaluated from these equations, thereby providing the necessary data to estimate the solubility and speciation of gold in H_2S -bearing vapours.

Chapter 3

PVTx properties of H₂O-H₂S fluid mixtures at elevated temperature and pressure based on new experimental data.

Denis Yu. Zezin, Artashes A. Migdisov, Anthony E. Williams-Jones

3.1. ABSTRACT

The volumetric properties of H_2O-H_2S fluid mixtures were determined experimentally at temperatures of 150 to 400 °C and pressures up to 240 bar. Using these data and existing equations of state, we developed a thermodynamic model for H₂O-H₂S fluid mixtures. This model is based on an asymmetric description of phases, which includes an activity model and a P-T-dependent Henry's law constant for the liquid, and equations of state with mixing rules for the vapour. The fugacity of the vapour was calculated using the cubic equations of state of Peng and Robinson (1976) and Patel and Teja (1982) with density-dependent and composition-dependent mixing rules. Sets of binary interaction parameters for these equations were fitted to the experimental data obtained in this study and supplemented by high-temperature PVTx data for H₂O-H₂S fluid mixtures reported in the literature. Pressure in the field of vapour and along the liquid-vapour boundary was estimated using the above equations of state with corresponding binary interaction parameters and a thermodynamic model for vapour-liquid equilibrium. The errors in the estimated pressure of the homogeneous vapour mixtures (average relative deviation from the experimentally determined pressure) were relatively low, ~ 5 to 8%. However, the errors were significantly higher for the estimated pressure of vapour saturated with liquid, i.e., along the vapour-liquid phase boundary (11 to 15%), due to the highly non-ideal behaviour of fluids comprising mixtures of polar components like H₂O and H₂S. The results of this study make it possible to reliably estimate the volumetric properties of aqueous fluids containing H₂S at temperatures and pressures up to 400 °C and 240 bar, i.e., for conditions commonly encountered in hydrothermal systems.

3.2. INTRODUCTION

Knowledge of the properties and behaviour of H₂O-H₂S fluid mixtures is essential in a number of geoscientific and engineering fields. Oil and natural gas refining, petroleum reservoir engineering, geothermal energy, hydrometallurgy and the production of heavy water may involve hydrogen sulphide as a reagent or by-product (Carroll, 1990). At elevated temperature, this system is important in a variety of geological environments. Hydrogen sulphide is the dominant sulphur species in many metamorphic, magmatic-hydrothermal and geothermal fluids, and commonly plays a pivotal role in controlling redox conditions, and in the formation of metallic mineral deposits.

In liquid-dominated hydrothermal systems, one of the important properties of H_2S , or more specifically its conjugate base, HS⁻, is its ability to form stable complexes with soft metals (metal cations that can be easily polarized) like Au⁺, e.g., Au(HS)^o and Au(HS)₂⁻ (Stefansson and Seward, 2004). This ability is widely considered to make H_2S an important agent of metal transport in hydrothermal ore-forming systems and, in the case of gold, the dominant agent of metal transport for deposits forming at temperatures below 350 °C (Williams-Jones et al., 2009). In magmatic hydrothermal systems, vapour can be an important and even dominant fluid, and a case has been made that this phase may also be important in transporting ore metals (Williams-Jones and Heinrich, 2005). As H₂S partitions strongly into the vapour, consideration has been given to the possibility that this species may be involved directly in the transport process. To this end, Zezin et al. (2007 and 2008) have investigated the solubility of gold in H₂S and H₂O-H₂S gas mixtures. These studies have demonstrated enhanced dissolution of gold as a result of the

formation of AuS or AuHS gas species and their solvation by H_2S and H_2O . To quantitatively evaluate these data and model the transport of gold in vapour-dominated hydrothermal systems, reliable information is required on the properties of H_2O-H_2S gas mixtures at elevated temperature and pressure.

At present, there is lack of experimental data with which to predict the *PVTx* properties (*PVTx* refers to pressure, volume, temperature and composition of liquid and vapour phases) of H₂O-H₂S gas mixtures at the conditions of interest for hydrothermal geochemistry. Although experimental measurements of the properties of these mixtures have been made for temperatures above 200 °C, with one exception, the data are restricted to low partial pressures of H₂S (e.g., Kozintseva, 1964; Suleimenov and Krupp, 1994). The only study of the H₂O-H₂S system at high pressure and high concentration of hydrogen sulphide was that of Gillespie and Wilson (1982), who presented limited pressure-temperature-composition data for three isotherms, 204, 260 and 315 °C. Consequently, existing equations of state are unable to reliably predict the properties of H₂O-H₂S gas mixtures in either the vapour-only field or along the vapour-liquid phase boundary.

In this paper, we report the results of experimental measurements designed to investigate the *PVTx* properties of H_2O-H_2S fluid mixtures in both the vapour-only field and along the vapour-liquid boundary at elevated temperature and pressure, and for a wide range of composition. Based on these data, we propose mixing rules and binary interaction parameters for equations of state that permit accurate calculation of the *PVTx* properties of H_2O-H_2S fluid mixtures in the field of vapour and along the vapour-liquid boundary. These mixing rules will greatly extend the applicability of existing equations of

state and will facilitate reliable modeling of processes involving H_2S -bearing aqueous vapour to a temperature of 400 °C.

3.3. PREVIOUS STUDIES OF THE SYSTEM H₂O-H₂S

Fluids in the system H_2O-H_2S belong to the Type III fluid class based on the classification of van Konynenburg and Scott (1980) because they are characterized by an interrupted locus of critical points. Consequently, the critical locus is described by two critical curves. One of these curves starts at the critical point of pure H₂O and, with progressive addition of H_2S to the system, moves to sharply higher pressure and lower temperature. The other critical curve starts at the critical point of pure H₂S and, with addition of H₂O, moves to higher pressure and temperature, and a critical end point corresponding to the termination of the three phase (liquid-liquid-vapour) boundary. Other characteristic features of this system are the existence of a liquid-liquid immiscibility gap and the formation of H₂O-H₂S gas hydrates at low temperature. The properties of the H₂O-H₂S system at temperatures below 150 °C will not be discussed in detail in this paper and readers interested in the behaviour of fluids in the system at such temperatures are therefore referred to other sources for this information (e.g., Carroll, 1990). At higher temperature, the mixture undergoes phase separation into a denser aqueous liquid and a less dense, H₂S-dominated vapour. However, the conditions at which these phase changes occur have not been constrained. According to Alekhin and Sretenskaya (1983), the behaviour of the H₂O-H₂S system is similar to that of the systems, water-carbon dioxide, water-ethane, water-methane and mixtures of water with

heavier hydrocarbons. By making comparisons to these other systems, it is therefore possible to semi-quantitatively estimate conditions of phase stability in the H₂O-H₂S system for pressures and temperatures not investigated experimentally.

Numerous experimental studies have investigated the solubility of H_2S in water and phase relations at the conditions of vapour-liquid equilibrium in the system H_2O-H_2S but, with rare exception, only at low temperature and low partial pressure of H_2S (Winkler, 1906; Wright and Maass, 1932; Selleck et al., 1952; Pohl, 1961; Kozintseva, 1964; Clarke and Glew, 1970; Lee and Mather, 1977; Drummond, 1981; Gillespie and Wilson, 1982; Barret et al., 1988; Carroll and Mather, 1989; Suleimenov and Krupp, 1994; Chapoy et al., 2005). These studies have led to a number of comprehensive models for the calculation of the volumetric properties of fluids and conditions of vapour-liquid equilibrium in the system H_2O-H_2S (Evelein et al., 1976; Carroll and Mather, 1989; Carroll and Mather, 1993; Chapoy et al., 2005; Dubessy et al., 2005; Duan et al., 2007; Perfetti et al., 2008; dos Ramos and McCabe, 2010).

The properties of two-phase fluid mixtures containing supercritical components (as in the case of hydrogen sulphide) are usually modeled using an asymmetrical approach, in which the vapour phase is described with an equation of state (EOS) that accounts for non-ideality with fugacity coefficients, and the liquid phase is described using activity coefficients (Reid et al., 1987). A wide variety of empirical and semi-empirical equations of state are available to calculate the volumetric properties of vapours and their stability relationships (Anderko, 1990). The Henry's law constant is employed to calculate the fugacity of the volatile, non-aqueous, components in the liquid. In this approach, accurate description of the properties of the vapour also requires the

availability of a suitable equation of state, i.e., one developed for the system of interest based on experimental determinations of the properties of the vapour in the mixture for a wide range of *PVTx* conditions.

Some researchers have also used equations of state to model the properties of the liquid (Evelein et al., 1976; Chapoy et al., 2005; Duan et al., 2007). In principle, the advantage of this approach is its simplicity in that the properties of both vapour and liquid are described by a single equation, which can be applied for a wide range of temperature and pressure. Nevertheless, because of the complex behaviour of fluids in the H₂O-H₂S system (this results from molecular association and dipolar interactions), it is not feasible to consider modeling the properties of vapour and liquid in this system using the same equation of state, particularly at elevated temperature, and for more complex natural systems in which salts are dissolved primarily in the liquid.

3.4. EXPERIMENTAL METHOD

Experiments involved in situ determination of the pressure developed by H_2O-H_2S mixtures of variable composition, and were performed in a constant-volume titanium cell (Grade 2 and VT1-0). Pressure was measured using a sapphire pressure-sensor connected to the cell (autoclave) through a custom-designed mercury-filled transducer, which was attached to the head-cap of the autoclave. The transducer consists of a custom-made titanium-foil membrane (11 mm diameter, 0.127 mm thickness) and titanium tubing (1/16" outer diameter) filled with mercury as a transmitting fluid (Fig. 3.1). The essential part of the transducer is the membrane, which separates a transmitting fluid from the



Figure 3.1. A sketch of the experimental setup for the measurement of the pressures of H_2O-H_2S fluid mixtures.

experimental fluid mixture. This membrane is flexible enough to compensate for the thermal expansion of mercury and yet resistant to corrosion at the conditions of the experiments. The voltage output from the sensor was converted to pressure units (bar) using the standard calibration for an HPLC pump and a commercially available high-precision pressure sensor (model PX409 purchased from Omega[®], accuracy 0.08%, NIST traceable calibration). All parts of the experimental apparatus constructed of titanium, including the pressure membrane, were reacted with nitric acid at 450 °C to form a protective layer of TiO₂, which would be resistant to the extremely corrosive H₂S-bearing fluids. The total volume of the autoclave (33 to 39 cm³) was determined by filling it with Milli-Q water at 25 °C, and weighing the whole autoclave assembly before and after filling, to an accuracy of ± 10 mg. Upon heating to 400 °C, the thermal expansion of titanium can reach 0.3%, which will lead to an increase of the volume of an autoclave of 0.4 cm³. Therefore, this expansion imposes an additional uncertainty of up to 1.1% on the value of the measured volume.

Pressure readings were taken at selected temperatures as the system attained equilibrium along heating and cooling paths. The difference between the pressure measured on heating and that on cooling was generally <0.4 bar. The average of the two pressure readings was considered to be the experimental pressure. Equilibrium was considered to have been attained when the measured pressure varied by less than 0.2 bar per hour. The precision of the measurements was ± 0.2 bar and therefore the total uncertainty of the measurements was less than 0.4 bar. Experiments were performed at temperatures between 150 and 400 °C in an electric oven (Fisher Isotemp[®] model 550-126) equipped with an aluminium box in which the autoclave was placed to reduce the

temperature gradient. In addition, the cell was placed in a sand bath to ensure uniform heating and cooling. The vertical temperature gradient measured with two chromel-alumel thermocouples located at the top and bottom of the oven was less than 0.5 °C/m. A thermal controller allowed the temperature fluctuations in the oven to be limited to ± 0.2 °C.

Milli-Q deionized distilled water, used to prepare the experimental mixture, was boiled for about an hour in a flow of nitrogen gas in order to remove dissolved atmospheric gases. Hydrogen sulphide gas was produced in the laboratory in a Kipp'stype apparatus by the reaction:

$$Na_2S + 2HCl = 2NaCl + H_2S \tag{1}$$

The H₂S gas was purified by passing it through two gas-washing bottles filled with Milli-Q water and then through a series of four cold traps to remove condensable gases such as water vapour. The cold traps cooled the H₂S to a temperature of -50 °C (using a mixture of solid CO₂ (dry ice) and methanol). Hydrogen sulphide produced and cleaned in the manner described above is considered to be ~99.8% pure by weight, based on analyses reported in Migdisov et al. (1998).

Prior to conducting an experiment, the autoclave was purged with nitrogen gas (for about 30 minutes) and with H_2S gas (for approximately 10 minutes) to expel the atmospheric gases and nitrogen. An aliquot of water was then introduced into the autoclave, and liquid H_2S condensed into it from a flow of purified gas by cooling the autoclave to a temperature below -70 °C. The mass of hydrogen sulphide in each experimental mixture was calculated from the mass of the empty autoclave, the mass of the water introduced and the mass of the autoclave after addition of H_2S . In order to

ensure that there was no reaction of hydrogen sulphide with the water during an experiment, for some runs, the mass of hydrogen sulphide was also determined after the experiment. The amount of H_2S in the cell after the runs was obtained by collecting the hydrogen sulphide on a cadmium acetate trap and precipitating it as CdS. The mass of H_2S was calculated from the weight of the washed (with distilled water) and dried CdS. The average difference between the initial and final masses of H_2S was 5.3% of the total mass (standard deviation 3.9%, based on 13 experiments); differences were both positive and negative. This indicates that any reaction between H_2S and H_2O was insignificant.

3.5. RESULTS AND TREATMENT OF EXPERIMENTAL DATA

3.5.1. Experimental Results

The results of the experimental measurements of the properties of H_2O-H_2S fluid mixtures are presented in Tables 3.1 and 3.2. A total of 44 experiments were conducted for conditions in the vapour-only region. Pressures were measured at temperatures from 250 to 400 °C for fluid mixtures ranging in composition (mole fraction of H_2S) from 0.09 to 0.73 (Table 3.1). These pressures ranged from 80 to 240 bar. A further 77 experiments were conducted for conditions at which the vapour was saturated with liquid at temperatures from 150 to 325 °C (Table 3.2). Most of these experiments were carried out at the following temperatures: 150, 171, 200, 225, 250, 275, 300 and 325 °C. The bulk composition of the fluid mixtures ranged from 0.04 to 0.73 and the corresponding pressure from 9 to 200 bar.

<i>T</i> °C	P, bar	$V, \text{ cm}^3$	H ₂ O, mole	H ₂ S, mole
250	123.1	37.8	0.056	0.107
250	80.5	37.8	0.056	0.050
250	96.6	37.9	0.056	0.070
250	114.8	33.1	0.056	0.077
250	164.5	33.1	0.055	0.147
275	124.6	33.1	0.056	0.077
275	183.2	33.1	0.055	0.147
300	149.9	37.8	0.056	0.107
300	98	37.8	0.056	0.050
300	154.9	38.1	0.139	0.076
300	164.3	33.1	0.139	0.074
300	108.5	33.1	0.139	0.026
300	134.5	33.1	0.056	0.077
300	72.7	33.1	0.056	0.021
300	202	33.1	0.055	0.147
300	154.5	33.1	0.083	0.080
300	172.1	33.1	0.112	0.093
300	114.4	33.1	0.112	0.031
325	114.4	37.8	0.056	0.050
325	173.8	38.1	0.139	0.076
325	136.9	38.1	0.219	0.020
325	187.3	33.1	0.139	0.074
325	137.4	33.1	0.139	0.026
325	145.6	33.1	0.056	0.077
330	145.9	38.1	0.219	0.020
350	191.5	38.1	0.139	0.076
350	169.6	38.1	0.219	0.020
350	146.8	38.4	0.556	0.030

Table 3.1. Results of experiments conducted in the region of homogeneous vapour.

<i>T</i> °C	<i>P</i> , bar	V, cm ³	H ₂ O, mole	H_2S , mole
350	239	38.5	0.333	0.085
350	207.7	33.1	0.139	0.074
350	153.6	33.1	0.139	0.026
350	194.5	33.1	0.278	0.046
350	156.9	33.1	0.056	0.077
350	173.9	33.1	0.083	0.080
350	215.9	33.1	0.112	0.093
350	125.9	33.1	0.112	0.031
365	219.8	33.1	0.139	0.074
365	162.8	33.1	0.139	0.026
365	203.7	33.1	0.278	0.046
365	164.1	33.1	0.056	0.077
365	182.5	33.1	0.083	0.080
375	186.1	33.1	0.083	0.080
400	183.3	33.1	0.139	0.026
400	177.1	33.1	0.056	0.077

Table 3.1. (continued)
Table 3.2. Results of experiments conducted for conditions of vapour-liquid equilibrium. The compositions of liquid and vapour were calculated by modeling the bulk fluid composition using the Stryjek-Vera modification of the Peng-Robinson equation of state (Peng and Robinson, 1976; Stryjek and Vera, 1986) in conjunction with the densitydependent mixing rules of Panagiotopoulos (1986).

measured (experimental data)				calculated		
<i>T</i> °C	P, bar	$V, \text{ cm}^3$	H ₂ O, mole	H ₂ S, mole	x_{H_2S}	\mathcal{Y}_{H_2S}
150	62.3	33.1	0.139	0.074	0.0218	0.8973
150	25.4	33.1	0.139	0.026	0.0092	0.7956
150	9	33.1	0.139	0.006	0.0020	0.4692
150	21.2	33.1	0.056	0.021	0.0074	0.7604
150	97.7	33.1	0.055	0.147	0.0303	0.9170
150	64.5	33.1	0.083	0.080	0.0225	0.8994
150	73.8	33.1	0.112	0.093	0.0250	0.9068
150	30.6	33.1	0.112	0.031	0.0112	0.8256
150	28.9	33.1	0.557	0.026	0.0106	0.8170
171	57	37.9	0.056	0.070	0.0185	0.8238
171	103.3	38.2	0.333	0.145	0.0304	0.8733
171	68.5	38.5	0.333	0.085	0.0219	0.8441
171	47	38.6	0.222	0.056	0.0153	0.7970
171	69.5	33.1	0.139	0.074	0.0222	0.8455
171	29.8	33.1	0.139	0.026	0.0091	0.7057
171	12.2	33.1	0.139	0.006	0.0019	0.3366
171	46.8	33.1	0.278	0.046	0.0152	0.7964
171	70.1	33.1	0.056	0.077	0.0224	0.8464
171	80.7	33.1	0.557	0.079	0.0252	0.8569
172	25.1	33.1	0.554	0.018	0.0072	0.6504
200	93.6	37.8	0.056	0.107	0.0271	0.7716
200	53.9	37.8	0.056	0.050	0.0154	0.6704

Chapter 3. - PVTx properties of H₂O-H₂S fluid mixtures

14010 3.2. (commaca)					
<i>T</i> °C	P, bar	$V, \text{ cm}^3$	H ₂ O, mole	H ₂ S, mole	x_{H_2S}	y_{H_2S}
200	67.5	37.9	0.056	0.070	0.0198	0.7203
200	33.6	38.1	0.219	0.020	0.0079	0.5147
200	121.3	38.2	0.333	0.145	0.0333	0.7963
200	79.9	38.5	0.333	0.085	0.0235	0.7497
200	53.7	38.6	0.222	0.056	0.0153	0.6695
200	82	33.1	0.139	0.074	0.0241	0.7536
200	38	33.1	0.139	0.026	0.0096	0.5631
200	19.3	33.1	0.139	0.006	0.0019	0.2012
200	57.3	33.1	0.278	0.046	0.0166	0.6853
200	82.5	33.1	0.056	0.077	0.0242	0.7546
200	32.1	33.1	0.056	0.021	0.0073	0.4951
200	127.6	33.1	0.055	0.147	0.0345	0.7995
200	84.5	33.1	0.083	0.080	0.0247	0.7580
200	96.6	33.1	0.112	0.093	0.0278	0.7754
200	44	33.1	0.112	0.031	0.0119	0.6131
200	41.3	33.1	0.557	0.026	0.0109	0.5924
205	34.6	33.1	0.554	0.018	0.0077	0.4797
225	81.3	37.9	0.056	0.070	0.0217	0.6214
225	95.7	33.1	0.139	0.074	0.0258	0.6580
225	48.5	33.1	0.139	0.026	0.0102	0.4424
225	28.4	33.1	0.139	0.006	0.0016	0.1132
225	69.3	33.1	0.278	0.046	0.0178	0.5770
225	96.7	33.1	0.056	0.077	0.0261	0.6601
250	58.3	38.1	0.219	0.020	0.0087	0.2901
250	63.7	38.4	0.556	0.030	0.0109	0.3384
250	157.9	38.2	0.333	0.145	0.0378	0.6097
250	110.6	38.5	0.333	0.085	0.0267	0.5464
250	62.7	38.6	0.222	0.056	0.0105	0.3301
250	113.3	33.1	0.139	0.074	0.0275	0.5523

Table 3.2. (continued)

Chapter 3. - PVTx properties of H₂O-H₂S fluid mixtures

1 aoit 5.2. (continueu)					
<i>T</i> °C	P, bar	$V, \text{ cm}^3$	H ₂ O, mole	H ₂ S, mole	x_{H_2S}	\mathcal{Y}_{H_2S}
250	62.8	33.1	0.139	0.026	0.0105	0.3309
250	41.8	33.1	0.139	0.006	0.0014	0.0605
250	85.6	33.1	0.278	0.046	0.0190	0.4677
250	115.9	33.1	0.083	0.080	0.0282	0.5577
250	129.7	33.1	0.112	0.093	0.0317	0.5814
250	70.8	33.1	0.112	0.031	0.0136	0.3899
250	67	33.1	0.557	0.026	0.0122	0.3638
262	134.1	33.1	0.557	0.079	0.0310	0.5190
264	63.9	33.1	0.554	0.018	0.0067	0.1960
275	181.9	38.2	0.333	0.145	0.0393	0.4905
275	132.3	38.5	0.333	0.085	0.0279	0.4336
275	135.5	33.1	0.139	0.074	0.0288	0.4401
275	82.5	33.1	0.139	0.026	0.0107	0.2370
275	108.9	33.1	0.278	0.046	0.0206	0.3686
300	103.9	38.1	0.219	0.020	0.0085	0.1306
300	108.3	38.4	0.556	0.030	0.0103	0.1549
300	211.6	38.2	0.333	0.145	0.0423	0.3375
300	161.2	38.5	0.333	0.085	0.0287	0.3176
300	136	33.1	0.278	0.046	0.0209	0.2636
300	113	33.1	0.557	0.026	0.0123	0.1783
304	174.9	33.1	0.557	0.079	0.0310	0.3085
310	116.7	38.1	0.219	0.020	0.0082	0.1052
316	191.7	33.1	0.557	0.079	0.0297	0.2142
325	136.3	38.4	0.556	0.030	0.0060	0.0572
325	198.2	38.5	0.333	0.085	0.0348	0.2339
325	168.5	33.1	0.278	0.046	0.0184	0.1437

Table 3.2. (continued)

3.5.2. Data Treatment

3.5.2.1. The Vapour-Only Region

The *PVTx* data collected in this study for the vapour-only region were modeled by equations of state (equations which correlate the pressure, temperature, volume and composition of a fluid; EOS), and the model pressures compared to those measured experimentally. Two types of EOS were used, the cubic, two-parameter Peng-Robinson EOS (Peng and Robinson, 1976), including its modification by Stryjek and Vera (1986), and the cubic, three-parameter Patel-Teja EOS (Patel and Teja, 1982). These EOS (referred to hereafter as the PR, PRSV and PT EOS) are the simplest and most widely used, and have been shown to reliably describe the PVTx properties of water vapour and hydrogen sulphide, the end-member fluids considered in this study. Thus, for example, the values of average absolute deviations of predicted saturated vapour and liquid densities for H₂O and H₂S are less than 2-3% for the PT EOS, and those of the vapour pressure are about 0.3 and 0.1% for PRSV and PT EOS, respectively (Stryjek and Vera, 1986; Patel and Teja, 1982). As the H₂O-H₂S system contains polar and associated components, in addition to simple classical quadratic mixing rules, we applied composition-dependent Redlich-Kister or Margules-type mixing rules (Lee et al., 1999; Anderko, 2000) and density-dependent mixing rules (Panagiotopoulos, 1986; Lee and Sandler, 1987). Furthermore, because H₂O-H₂S fluids are highly non-ideal, binary interaction parameters (BIPs), which permit modification of the attractive term of the equation, were used to introduce flexibility into the EOS needed to accurately describe their PVTx properties (Anderko, 1990). The complete forms of these EOS and their mixing rules, as well as the expression for calculating fugacity coefficients, can be found in the Appendix.

3.5.2.2. The Vapour-Liquid Region

In order to model the conditions of vapour-liquid equilibrium and adjust the BIPs of the EOS describing the properties of the vapour in the two-phase region, it was also necessary to evaluate the composition and distribution of the coexisting phases from the measured temperature, pressure, volume and bulk molar composition of the fluid mixture. The pressures estimated using the resulting thermodynamic equilibrium model were compared to those measured in the experiments.

As hydrogen sulphide is a supercritical fluid in the H₂O-H₂S system at the conditions of our experiments (\geq 150 °C), we used an asymmetrical approach to model the properties of the fluids and calculate the composition of the coexisting phases. For conditions at which the system contained a liquid, the fugacities of components in this phase were calculated using a model in which thermodynamic equilibrium in the mixture was constrained by the following two equations (Reid et al., 1987):

$$y_{H_{2O}} \cdot \varphi_{H_{2O}} \cdot P = \gamma_{H_{2O}} \cdot x_{H_{2O}} \cdot P_{H_{2O}}^{vp} \cdot \varphi_{H_{2O}}^0 \cdot \exp \int_{P^{vp}_{H_{2O}}}^{P} \frac{v_{H_{2O}}^{liq}(T, P)dP}{RT}$$
(2)

$$y_{H_2S} \cdot \varphi_{H_2S} \cdot P = \gamma_{H_2S} \cdot x_{H_2S} \cdot K_{H_2S} (T, P)$$
(3)

In these equations, *P* is the pressure, *x*, *y* are the concentrations (mole fractions) of H₂O or H₂S in the liquid and vapour, respectively, φ is the fugacity coefficient of H₂O or H₂S in

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the mixture calculated from an equation of state, γ is the activity coefficient of H₂O or H₂S in the liquid, and $K_{H_2S}(T, P)$ is the Henry's law constant (the value of $K_{H_2S}(T, P)$ used in the calculations was selected to be consistent with concentration units). The product $P_{H_2O}^{vp} \cdot \varphi_{H_2O}^0 \cdot \exp \int_{P^{\varphi}_{H_2O}}^{P} \frac{v_{H_2O}^{hq}(T, P)dP}{RT}$ represents the fugacity of liquid water at a pressure *P* and temperature *T*, $\varphi_{H_2O}^0$ and $P_{H_2O}^{vp}$ are the fugacity coefficient and the vapour pressure of pure H₂O at liquid saturation, respectively; the exponential term is the Poynting factor containing the molar liquid volume of H₂O and $v_{H_2O}^{hq}$, and *R* is the gas constant. The values of the saturated vapour pressure, $P_{H_2O}^{vp}$, and the liquid molar volume of pure water, $v_{H_2O}^{hq}$, were calculated using the approximation of Saul and Wagner (1987), and the fugacity coefficient of pure water, $\varphi_{H_2O}^0$, calculated from the equation of Li and

Nghiem (1986). The Henry's law constant, $K_{H_2S}(T, P)$, was calculated as a function of temperature and pressure from the model proposed by Majer et al. (2008).

The following modified version of the extended Debye-Huckel equation (Helgeson et al., 1981) containing the salting-out Setchenow coefficient was used to calculate the activity coefficients of components in the aqueous liquid:

$$\log \gamma_i = \frac{-A \cdot z_i^2 \cdot \sqrt{I_a}}{1 + B \cdot \mathring{a}_i \cdot \sqrt{I_a}} + \Gamma_{\gamma} + s \cdot I_a$$
(4)

where I_a is the apparent ionic strength of a solution, z_i the electrical charge of a component, A and B are constants, a_i is the distance of closest approach, Γ_{γ} is the mole fraction converted from molality ($\Gamma_{\gamma} = -\log (1 + 0.0180153 \cdot m')$, where m' is the sum of

the molalities of all solute species, and *s* is the Setchenow coefficient calculated from the correlation given in Suleimenov and Krupp (1994).

As H₂S is a weak acid, it dissolves in pure water dominantly as the neutral solute H₂S and displaces the pH of the solution only to moderately acidic conditions (pH~3-4); the proportion of HS⁻ is estimated to be $<2.5 \cdot 10^{-3}$ mol%. For this reason, a truncated version of equation 4 containing only the second and third terms can be used to describe the behaviour (activity coefficient) of H₂S in water.

3.5.2.3. Optimization Procedure

The properties of vapour and liquid at conditions of equilibrium of the two phases were evaluated iteratively using the algorithm described in Figure 3.2. The procedure for obtaining the properties of these two phases and optimizing the parameters of the EOS was based on Duhem's theorem, which states that a closed system at equilibrium is completely defined if the initial sum of the molar amounts of the components and two other independent variables are specified (Smith et al., 2001). In the main cycle of the algorithm, the BIPs were fitted for every isothermal dataset. Thus, from the measured temperature and pressure, and initial guesses of the BIPs for the mixing rules of the EOS considered at the bulk molar composition of interest, we were able to calculate the composition and distribution of the phases iteratively. These parameters were adjusted in the same algorithm to ensure that the system obeyed the thermodynamic conditions of equilibrium, namely that each component of each phase is at the same temperature, pressure and chemical potential (or fugacity) in both phases.

Figure 3.2. Diagrammatic representation of the algorithm used to calculate equilibrium compositions for the system H_2O-H_2S in the two-phase region.

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The compositions of liquid and vapour and the molar distribution of H_2O and H_2S were calculated from the measured total volume of the system using equations 2 and 3, and initial guesses of the binary interaction parameters of the EOS. These data, in turn, were used to determine the molar volumes of H_2O and H_2S in the liquid and vapour using the following relationships:

$$v^{liq} = \sum x_i \cdot v_i^{liq} \tag{5}$$

$$v^{vap} = \frac{V - v^{liq} \cdot N^{liq}}{N^{vap}} \tag{6}$$

where *V* is the total volume and N^{liq} and N^{vap} are the total number of moles in the liquid and the vapour, respectively. The partial molar volume of H₂S, $v_{H_2S}^{liq}$, was calculated from the model of Sedlbauer et al. (2000) assuming that at temperatures of up to 325 °C and low concentrations of an essentially molecular solute, it can be approximated as a standard partial molar volume. A convergence between this calculated molar volume of the vapour and that calculated from the EOS using initially guessed BIPs in the internal cycle of the algorithm, ensured that the EOS described the properties of the vapour phase with acceptable accuracy.

Sets of two-phase compositional data and binary interaction parameters for the EOS were calculated iteratively using the Simplex minimization algorithm (MATLAB[®] software) and appropriate mixing rules. Since an accurate description of the volumetric properties of a fluid is essential in the geosciences (e.g., for determining the physicochemical conditions of trapping of fluid inclusions in minerals or estimating the metal-transporting capacity of hydrothermal fluids) and pressure was the measured parameter, the objective function contained residuals of pressure calculated from the EOS

(single-phase data) and the vapour-liquid equilibrium boundary (the two-phase dataset; equations 2 and 3).

Using the experimental data obtained in this study and the experimental measurements reported by Suleimenov and Krupp (1994), we were able to derive an optimum set of BIPs for a wide range of temperature and partial pressure of H_2S . The BIPs for each EOS were fitted to the properties and composition of both liquid-undersaturated and -saturated vapour. As a result, the entire calculation procedure satisfied the conditions required for equilibrium between liquid and vapour, and the model for vapour-liquid equilibrium developed using the EOS with mixing rules and binary interaction parameters is applicable anywhere in the heterogeneous region covered by this study. Finally, the pressures estimated from the model for the two-phase boundary and for the vapour-only region reproduce the measured pressures.

3.5.3. Calculated Fluid Compositions and Binary Interaction Parameters

In Table 3.2, we report the calculated compositions of the coexisting liquid and vapour along the two-phase boundary together with the measured temperatures, pressures, volumes and bulk compositions of the mixture. The compositions of liquid and vapour on the two-phase boundary varied with the choice of the EOS used to estimate fugacity coefficients, and this difference increased with increasing temperature and pressure of H_2S . The mole fraction of H_2S in the vapour determined using the PT EOS is somewhat lower than that determined using the PR EOS, despite the fact that both models accurately describe the volumetric properties of the fluid. However, the latter model provides better

agreement with the experimental data reported in the literature (Selleck et al., 1952; Gillespie and Wilson, 1984). In view of this and the fact that the results estimated from the PR EOS are independent of the mixing rules chosen, the binary interaction parameters in the various EOS tested were evaluated using the compositions of liquid and vapour calculated using the PR EOS. A temperature-dependence for all sets of BIPs was established for the different EOS and their corresponding mixing rules (Fig. 3.3).

3.6. DISCUSSION

The most important conclusion that can be drawn from Figure 3.3 is that the temperaturedependence of the BIPs is strongly affected by the mixing rules employed. In the case of the PRSV EOS, the classic quadratic mixing rules and the Lee-Sandler density-dependent mixing rules both yield BIPs that can be accurately represented as simple monotonic functions of temperature; the functions for k_{12} and k_{21} are parallel in both cases, and with the Lee-Sandler mixing rules are also nearly linear. (Fig. 3.3 a, b). If the densitydependent mixing rules of Panagiotopoulos (1986) are applied to the PRSV EOS (Fig. 3.3 c), the behaviour of the first binary interaction parameter, k_{12} , which is unrelated to density (or molar volume), resembles that of the BIPs calculated using simple quadratic mixing rules. In contrast, the second parameter c_{21} , which is strongly affected by molar volume, shows inconsistent behaviour at temperatures above about 300 °C (Fig. 3.3 c). This may be related to the precipitous drop in the density of aqueous liquid as the system approaches the critical temperature of H₂O. We also note that the form of this densitydependent mixing rule leads to a decrease in the contribution of the density term with Figure 3.3. Diagrams showing the temperature dependence of binary interaction parameters for the Peng Robinson equation of state modified by Stryjek and Vera (1987; PRSV) and the Patel-Teja equation of state (Patel and Teja, 1982) for density-and composition-dependent mixing rules. The symbols represent binary interaction parameters fitted to isothermal experimental datasets; the lines are least-square estimates provided by the equations listed in Table 3.3. PRSV (CLAS) refers to classical quadratic mixing rules applied to the PRSV EOS; PRSV (COMP) – Margules-type composition dependent mixing rules (Anderko, 2000) applied to the PRSV EOS; PT (COMP) – composition dependent mixing rules applied to the PT EOS (Lee et al., 1999); PR LS (DD) – Lee-Sandler density dependent mixing rules (Lee and Sandler, 1987) applied to the PRSV EOS; PR Pan (DD) – Panagiotopoulos density dependent mixing rules applied to the PRSV EOS (Panagiotopoulos, 1986).



Table 3.3. Polynomial fits of binary interaction parameters (BIPs) as a function of temperature, and comparisons of experimentally-determined pressures to pressures calculated using selected equations of state with optimized BIPs for classic quadratic, density- and composition-dependent mixing rules (see text for abbreviations).

EOS (Mixing rules)	BIPs $\frac{P_{EXP} - P_{CAI}}{P_{EXP}}$			<u>^{LC}</u> ·100%	
		total	V	V+L	
PRSV (CLAS)	$k_{12} = -4.0691 + 4005.9T^{-1} - 932403T^{-2}$ $k_{21} = -7.8565 + 7319.7T^{-1} - 1685151T^{-2}$	12.8	8.2	15.1	
PRSV (COMP)	$k_{12} = 140.79 - 17213.9T^{1} - 251077T^{2} - 0.2697T + 1.57 \cdot 10^{-4}T^{2}$ $k_{21} = 237.99 - 50251.3T^{-1} + 2906270T^{-2} - 0.4374T + 2.77 \cdot 10^{-4}T^{2}$	10.9	6.3	12.9	
PR LS (DD)	$k_{12} = -0.7976 + 640.91T^{-1} - 116337T^{-2}$ $k_{21} = -0.94 + 479.62T^{-1} - 77109.8T^{-2}$	11.9	6.2	14.4	
PT (COMP)	$k_{12} = 3.9187 + 12346.9T^{-1} - 2631380T^2 - 0.754T + 7.7 \cdot 10^{-5}T^2$ $k_{21} = 214.16 - 24399.2T^{-1} - 4153826T^2 - 0.42536T + 2.6 \cdot 10^{-4}T^2$	11.3	6.6	13.6	
PR Pan (DD)	$k_{12} = -126.21 + 40903.5T^{-1} - 4991097T^{-2} + 0.17481T - 9.2 \cdot 10^{-5}T^{2}$ $c_{21} = 629.79 - 210344T^{-1} + 26108360T^{-2} - 0.82991T + 4.1 \cdot 10^{-4}T^{2}$	10.0	5.7	11.8	

T – temperature (K); V – single-phase (vapour) mixture, V+L – two-phase fluid mixture Applicable at temperatures from 423 to 673 K.

increasing molar volume (i.e., decrease of density). Thus, although this mixing rule performs well for fluids at high density and low temperature, it should be used with caution for water-bearing mixtures at temperatures above ~300 °C.

The behaviour of the BIPs as a function of temperature is more complex for composition-dependent mixing rules than it is for density-dependent mixing rules. Examples of composition-dependent mixing rules are Redlich-Kister-type rules, which have been used in conjunction with the PT EOS (Lee et al., 1999) and Margules-type rules, which have been used in conjunction with the PRSV EOS (Anderko, 2000; see Fig. 3.3 d, e). In both cases, the BIPs fluctuate between values of approximately 1 and -1. The k_{12} parameter has a marked maximum at a temperature of ~200 °C, and at higher temperature (over 300 °C) it changes its sign. The function for the k_{21} parameter exhibits a minimum between about 250 and 300 °C, but its behaviour at higher temperature is unclear.

The optimized temperature-dependent functions of the BIPs for density- and composition-dependent mixing rules for the PRSV and PT EOS, and the percentage of relative deviation of pressure calculated using these EOS from the measured pressure are reported in Table 3.3. The predictive capabilities of these equations with respect to the properties of the vapour in both homogeneous and two-phase fluids are illustrated in Figure 3.4. The difference between the experimentally measured and calculated pressures

is presented as an average relative deviation, i.e.,
$$\frac{1}{N} \sum \left(\frac{P_{EXP} - P_{CALC}}{P_{EXP}} \right| \cdot 100\%$$
, where *N* is the number of measurements along a particular isotherm. The large deviations for the two-phase fluids probably result from the fact that it was first necessary to calculate the compositions of vapour and liquid before calculating the properties of these fluids. This 105



Figure 3.4. Average relative deviations of the pressures calculated using equations of state with density- and composition-dependent mixing rules from those measured in our experiments. The upper cluster of curves represents the deviations for conditions at which vapour is in equilibrium with liquid, whereas the lower cluster shows deviations for homogeneous vapour. For details of the equations of state and abbreviations see the caption for Figure 3.3.

was unnecessary for the homogeneous vapour-only field, and consequently the pressures predicted from the EOS are much closer to the experimentally measured pressures; the average pressure deviations are 5-8%.

The greatest deviations in pressure for both the vapour-only and liquid-saturated fluid mixtures were obtained using classic mixing rules applied to the PRSV EOS (PRSV (CLAS) in Figure 3.4). Introduction of composition and density dependence in the attractive parameter of the mixing rules improved the performance of this EOS. When used in conjunction with composition-dependent mixing rules, both the PRSV and PT EOS (PRSV (COMP) and PT (COMP) in Figure 3.4; Anderko, 2000; Patel and Teja, 1982; Lee et al., 1999) reliably predict the properties of homogeneous vapour and vapour in equilibrium with liquid throughout the temperature range of interest. They also predict these properties more reliably than the PRSV EOS with Lee-Sandler density-dependent mixing rules (PR LS (DD) in Figure 3.4; Lee and Sandler, 1987) at temperatures up to about 300 °C, although not more reliably than the PRSV EOS with the density-dependent mixing rules of Panagiotopoulos (1986; PR Pan (DD) in Figure 3.4). Nevertheless, at higher temperature, the performance of the PR LS (DD) is significantly better, and predicts the measured pressures more reliably than do either the PRSV or PT EOS with composition-dependent mixing rules or the PRSV EOS with the density-dependent mixing rules of Panagiotopoulos (1986). Nonetheless, the mixing rules proposed by Panagiotopoulos (1986) are superior for calculations of the volumetric properties of vapour at equilibrium with liquid. In general, the non-ideality of the H₂O-H₂S asymmetric system, which is related to low-energy interactions (dipole-dipole or hydrogen bonding

that become more important at higher density, is best modeled using system-specific mixing rules incorporating molar volume (density) dependence (Fig. 3.4).

In Figure 3.5, we compare the pressures for binary H_2O-H_2S fluid mixtures determined experimentally in this study and in several earlier studies (Selleck et al., 1952; Gillespie and Wilson, 1984) with pressures calculated using the PRSV EOS and the density-dependent mixing rules of Panagiotopoulos (1986). As is evident from this figure, the modeled pressures and compositions agree well with most of the experimental data. However, deviations are observed for two high-pressure measurements of Gillespie and Wilson (1984) at 315 °C.

From the preceding discussion, it is apparent that the data obtained in our experiments can be used reliably to select the most appropriate EOS, fit the necessary adjustable binary interaction parameters, and generate a thermodynamic model that accurately describes the *PVTx* properties of H₂O-H₂S fluids in both homogeneous vapour and coexisting vapour and liquid. This model can be applied in numerical calculations designed to estimate volumetric properties of H₂S-bearing aqueous vapour in natural hydrothermal systems. It can also be used to evaluate the properties of H₂S-bearing vapour in experimental studies investigating the capacity of this vapour to transport metals at elevated temperature (up to 400 °C). The model provides estimates of the properties of two-phase fluid mixtures that are less accurate than those for vapour-only fluids because of the complexity of interactions between dipole molecules of H₂O and H₂S in the liquid phase. Nonetheless, the estimates are adequate to describe the properties of most natural and experimental two-phase fluids containing significant proportions of H₂S at temperatures above 150 °C.



Figure 3.5. Pressure-composition (mole fraction of liquid *x* or vapour *y*) diagram showing calculated phase relations in the system H_2O-H_2S and pressure-composition relations for selected isotherms determined by fitting the experimental data obtained in this study to the PRSV equation of state and the density-dependent mixing rules of Panagiotopoulos (1986). Also shown are previously published experimentally-determined pressures for different compositions in the system. The circles represent the data of Selleck et al. (1952) and the rhombs the data of Gillespie and Wilson (1984).

3.7. CONCLUSIONS

The lack of experimental data for mixtures of H₂O and H₂S at elevated temperature and high partial pressure of H₂S has precluded reliable modeling of the properties and phase relations in this system at conditions typically encountered in hydrothermal fluids. The results of this study provide the high temperature experimental data for both homogeneous vapour and vapour in equilibrium with liquid that are required for this modeling. These new data have permitted satisfactory regression of binary interaction parameters for existing equations of state to yield a set of equations that can be used for reliable quantitative determination of the behaviour and properties of homogeneous vapour and liquid-saturated vapour in the system H₂O-H₂S at temperatures from 150 to 400 °C. The most reliable prediction of the properties of these fluids at temperatures up to 300 °C is provided by the Peng-Robinson equation of state modified by Stryjek and Vera (1986) using the density-dependent mixing rules of Panagiotopoulos (1986). At higher temperature, a better fit to the experimental data is provided by the density-dependent mixing rules of Lee and Sandler (1987) used in conjunction with the same equation of state.

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APPENDIX

Equations of state:

PT - Patel and Teja EOS (1982):

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + c(v-b)}$$

Mixing rules:

Classical:

$$a = \sum_{i} \sum_{j} x_i x_j \left(a_i a_j \right)^{0.5} \left(1 - k_{ij} \right)$$

Note, here and below that the expressions for parameters a_i , b_i and c_i for the end-member components can be found in original papers cited below. The parameters b and c were calculated using simple linear rules:

$$b = \sum_{i} x_i b_i, \ c = \sum_{i} x_i c_i$$

Composition-dependent (Lee et al., 1999):

$$a = \sum_{i} \sum_{j} x_{i} x_{j} (a_{i} a_{j})^{0.5} [(1 - k_{ij}) - (x_{i} - x_{j}) k_{ji}]$$

PRSV - Peng-Robinson EOS (Peng and Robinson, 1976) modified by Stryjek and Vera (1986):

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)}$$

Mixing rules:

Classical:
$$a = \sum_{i} \sum_{j} x_{i} x_{j} (a_{i} a_{j})^{0.5} (1 - k_{ij})$$

Composition-dependent (e.g., Stryjek and Vera, 1986; Anderko, 2000):

$$a = \sum_{i} \sum_{j} x_{i} x_{j} (a_{i} a_{j})^{0.5} [1 - (k_{ij} x_{i} + k_{ji} x_{j})]$$

Density-dependent (Panagiotopoulos, 1986):

$$a = \sum_{i} \sum_{j} x_{i} x_{j} (a_{i} a_{j})^{0.5} (1 - k_{ij}) + \frac{b}{RTv} \sum_{i} \sum_{j \neq i} x_{i} x_{j} [x_{i} c_{ij} + x_{j} c_{ji}], \text{ where } c_{ij} = -c_{ji}$$

PR EOS with Lee-Sandler density-dependent mixing rules (Peng and Robinson, 1976; Lee and Sandler, 1987):

$$P = \frac{RT}{v-b} - \frac{a \cdot f_a}{(v+\alpha b)(v+\beta b)}$$
$$f_a = \sum_i \sum_j x_i x_j \frac{(v+\alpha b)(v+\beta b)}{(v+\alpha b_{ij})(v+\beta b_{ij})} \frac{a_{ij}}{a}$$
$$\alpha = 1 + \sqrt{2}; \beta = 1 - \sqrt{2}$$

Fugacity coefficients are calculated using the general expression:

$$\ln \varphi_i = -\frac{1}{RT} \int_{V}^{\infty} \left[\left(\frac{\partial P}{\partial N_i} \right)_{T,V,N_{j \neq i}} - \frac{RT}{V} \right] dV - \ln Z$$

where φ_i , is the fugacity coefficient of the component *i* in the fluid mixture, *R* is the gas constant, *T* is the temperature, *V* is the total volume of the system, *P* is the vapour pressure, N_i – stands for the number of moles of a component *i* in the mixture, *Z* is the compressibility factor.

INTRODUCTION TO CHAPTER 4

Inasmuch as water is a dominant component of hydrothermal vapours and hydration can significantly enhance the solubility of metals in the gas phase, it follows that any study of the complexation of gold with reduced sulphur is incomplete without consideration of the contribution of hydration. Using the results of the experiments investigating the solubility of gold in pure H₂S presented in Chapter 2 and the study of the properties and behaviour of H₂O-H₂S fluid mixtures presented in Chapter 3, it is possible to evaluate the results of experiments designed to investigate the solubility and speciation of gold in H₂S-bearing water vapours. The equation of state for H₂O-H₂S gas mixtures permits evaluation of the fugacity coefficients of gas-solvent components and accounts for the non-ideal mixing of polar gases. The gold sulphide species may be expected to undergo hydration by H₂O via low-energy electrostatic interactions, in a similar manner to that of the solvation by H₂S gas molecules discussed in Chapter 2.

The experimental investigation of the solubility of gold in H_2S -bearing vapours presented in Chapter 4 constrains the stability and distribution of gold complexes in water vapour containing reduced sulphur. The study was conducted at a temperature from 300 to 365 °C and variable density and composition of the gas mixture. The solubility of gold in H_2O - H_2S gas mixtures is attributed to the formation of gold-sulphide species solvated by both H_2S and H_2O . The set of equilibrium constants determined for the dissolution reactions together with the solvation and hydration numbers for the gold species are used to estimate the optimal conditions for transporting gold in hydrothermal vapours. Chapter 4

The solubility of gold in H₂O-H₂S vapour at elevated temperature and pressure.

Denis Yu. Zezin, Artashes A. Migdisov, Anthony E. Williams-Jones

4.1. ABSTRACT

This experimental study sheds light on the complexation of gold in reduced sulphurbearing vapour, notably, in H₂O-H₂S gas mixtures. The solubility of gold was determined in experiments at temperatures of 300, 350 and 365 °C and reached 2.2, 6.6 and 6.3 μ g/kg, respectively. The density of the vapour varied from 0.02 to 0.22 g/cm³, the mole fraction of H₂S in the vapour varied from 0.03 to 0.96, and the pressure in the cell reached 263 bar. Statistically significant correlations of the amount of gold dissolved in the fluid with the fugacity of H₂O and H₂S permit the experimental data to be fitted to a solvation/hydration model. According to this model, the solubility of gold in H₂O-H₂S gas mixtures is controlled by the formation of sulphide or bisulphide species solvated by H₂S or H₂O molecules. Formation of gold sulphide species is statistically favoured over gold bisulphide species and thus the gold is interpreted to dissolve according to reactions of the form:

$$Au(s) + (n+1)H_2S(g) = AuS \cdot (H_2S)_n(g) + H_2(g)$$
(A1)

$$Au(s) + H_2S(g) + mH_2O(g) = AuS \cdot (H_2O)_m(g) + H_2(g)$$
(A2)

Equilibrium constants for reaction A1 and the corresponding solvation numbers (K_{A1} and n) were evaluated from the study of Zezin et al. (2007). The equilibrium constants as well as the hydration numbers for reaction A2 (K_{A2} , and m) were adjusted simultaneously by a custom-designed optimization algorithm and were tested statistically. The resulting values of log K_{A2} and m are -15.3 and 2.3 at 300 and 350 °C and -15.1 and 2.2 at 365 °C, respectively. Using the calculated stoichiometry and stability of reactions A1 and A2, it is now possible to quantitatively evaluate the contribution of reduced sulphur species to the

Chapter 4. - The solubility of gold in H₂O-H₂S vapour

transport of gold in aqueous vapour. This information will find application in modelling gold ore-forming processes in vapour-bearing magmatic hydrothermal systems, notably those of epithermal environments.

4.2. INTRODUCTION

It is now widely acknowledged that the gold deposited in ore-forming quantities by magmatic hydrothermal systems may be transported to the site of deposition by lowdensity supercritical aqueous fluids or vapours (Heinrich et al., 1999; Williams-Jones et al., 2002; Williams-Jones and Heinrich, 2005; Simon et al., 2007; Pirajno, 2009; Seo et al., 2009; Landtwing et al., 2010; Mavrogenes et al., 2010). The records of these hydrothermal systems are preserved as fluid inclusions and show, for shallow porphyry and high-sulphidation epithermal environments, that portions of these systems are invariably vapour-dominated (Heinrich et al., 2004; Redmond et al., 2004; Landtwing et al., 2010). Furthermore, analyses of the fluid inclusions indicate that commonly the concentration of gold is substantially higher in the vapour than in the coexisting brine (Ulrich et al., 1999; Seo et al., 2009; Pudack et al., 2009; Landtwing et al., 2010). This provides very strong evidence that the associated gold deposits have been formed in large part by magmatic vapour. However, our knowledge of the mechanisms by which gold is transported in the vapour and the physicochemical parameters that promote this transport is extremely poor. There is only very limited information on the nature of some of the volatile gold complexes that may be important and even less information on their stability for the conditions that may be of importance in gold transport. As a result, it is currently not possible to quantitatively assess the contribution of the vapour to the transport of gold during the formation of economic gold deposits, although qualitatively we may conclude that it is large.

<u>Chapter 4. - The solubility of gold in H₂O-H₂S vapour</u>

Several experimental studies have recently addressed the issue of the partitioning of gold between liquid and vapour at hydrothermal and magmatic conditions (Pokrovski et al., 2005 and 2008; Simon et al., 2007; Zajacz et al., 2010). The results of the studies of Simon et al. (2007) and Zajacz et al. (2010) clearly indicate that appreciable concentrations of gold can be extracted from the melt and dissolved in low-density fluids at high temperature and pressure. Pokrovski et al. (2008) concluded that, at lower temperature (350-500 °C), the vapour can contain between one and two orders of magnitude more gold than the coexisting liquid, and that this fractionation is largely driven by the presence of sulphur in the fluid. Nevertheless, these studies did not provide the data needed to quantitatively model gold transport. Information of this type was provided by Archibald et al. (2001) and Zezin et al. (2007), for temperatures between 300 and 400 °C and is applicable to epithermal and some porphyry environments (Williams-Jones and Heinrich, 2005). These experimental studies investigated the stability of chloride and sulphide complexes of gold in H₂O-HCl vapour mixtures and H₂S gas, respectively. The data revealed that gold forms stable chloride and sulphide species and that the solubility of the gold is increased by the formation of these complexes and a shell of oriented polar molecules (H₂O or H₂S) around the Au species. Although the study by Zezin et al. (2007) was restricted to the system Au-H₂S, the observation that solvation is important in this system as well as in the system Au-H₂O-HCl (hydration) suggests that solvation by H₂S and hydration may both be important factors in facilitating gold dissolution in natural H₂S bearing fluids, which are likely to be dominated by H₂O.

Predictably, the sulphur content of an aqueous fluid has a major positive impact on the solubility of gold and its fractionation between vapour and liquid (H₂S partitions

Chapter 4. - The solubility of gold in H₂O-H₂S vapour

preferentially into the vapour phase; Gammons and Williams-Jones, 1995), as has been shown recently for magmatic conditions (1000 °C) by Zajacz et al. (2010). These authors found that gold fractionates preferentially into the vapour and in increasing proportions with increasing sulphur content. Moreover, they found that alkali and alkali earth chlorides (NaCl, KCl, LiCl, CaCl₂) enhance the solubility of gold in H₂S-bearing vapours. Consistent with Zezin et al. (2007), they interpreted their experimental data to reflect, in part, the formation of $AuHS(H_2S)$; Zezin et al. (2007) concluded that Au solubility in the system Au-H₂S is controlled by the molecular species AuHS·(H₂S)_n or AuS·(H₂S)_n. In order to explain the positive correlation between gold solubility and alkali chloride concentration, Zajacz et al. (2010) also proposed that gold solubility in their experiments was partly controlled by the formation of species such as $(H_2S)_{0.5}$ -AuHS-(NaCl)_{0.5}. Finally, we note that ab initio molecular dynamic calculations performed for liquids and high-temperature lower density fluids (Pokrovski et al., 2009) confirm the linear geometry of the gold sulphide species Au(H₂S)HS and also Au(H₂O)HS. However, the calculations did not evaluate the stability of these species.

Although several studies have shown that complexation of Au with reduced sulphur enhances the solubility of this metal in low-density low-salinity vapour, only the study of Zezin et al. (2007) provides the thermodynamic data needed to evaluate gold solubility in vapour, and these were for the water-free system. Given the success of the solvation model in interpreting the solubility of a variety of metals in aqueous vapour (e.g., Migdisov and Williams-Jones, 2005; Rempel et al., 2006 and 2008; Zezin et al., 2007), it would be logical to expand the study of Zezin et al. (2007) by testing the role of hydration on the solubility of gold in H_2S -bearing systems. In this paper, we report results
of experiments designed to measure the solubility of gold in H_2O-H_2S gas mixtures at temperatures from 300 to 365 °C, evaluate models of gold speciation, and determine stability constants for the most plausible species.

4.3. METHOD

The method used in this study is similar to that described in previous experimental studies devoted to the solubility of metals in the gas phase (e.g., Migdisov et al., 1999; Archibald et al., 2001 and 2002; Zakaznova-Iakovleva et al., 2001; Migdisov and Williams-Jones, 2005; Rempel et al., 2006 and 2008; Zezin et al., 2007). The experiments were carried out in titanium-alloy autoclaves (Grade 2 and VT1-0) with volumes of ~30-40 cm³. Volumes were determined by filling the autoclaves with 25 °C distilled water and weighing them before and after filling. The weighing was performed to an accuracy of ± 10 mg.

The mixtures of fluids for the experiments were prepared directly in the autoclaves. Initially, the autoclaves were purged with nitrogen gas (for about 30 minutes) to expel the atmospheric gases. Aliquots of deionised Milli-Q water were introduced into an autoclave (reactor) at room temperature and then liquid H_2S (1-6 g) was added by condensing it out of a flow of purified gas cooled to a temperature below -70 °C. In order to remove dissolved atmospheric gases, the water used to prepare the experimental mixture was boiled for about an hour and then cooled in a stream of nitrogen gas. Hydrogen sulphide gas was produced in the laboratory in a Kipp's-type apparatus by the reaction:

$$Na_2S + 2HCl = 2NaCl + H_2S \tag{1}$$

The H₂S gas was purified by passing it through two gas-washing bottles filled with Milli-Q water and then through a series of four cold traps to remove condensable gases such as water vapour. The cold traps cooled the H₂S to a temperature of -50 °C (using a mixture of solid CO₂ and methanol). The H₂S produced and cleaned in the manner described above is considered to be ~99.8% pure by weight based on analyses reported in Migdisov et al. (1998).

A native gold wire (Alfa Aesar, 99.95% purity) was placed in each autoclave in a silica-glass ampoule. The ampoules were open at the top and stand well above the liquid, thereby isolating the solid from the liquid during heating or cooling. The redox potential of the system was controlled by adding pure elemental sulphur (Alfa Aesar, 99.5% purity) in amounts sufficient to maintain equilibrium between H₂S and S ($S+H_2=H_2S$) at the conditions of the experiments. This sulphur was placed in separate open silica-glass holders.

Experiments were performed at temperatures from 300 to 365 °C in an electric oven (Fisher Isotemp[®] models 818F and 550-126) equipped with an aluminum box in which autoclaves were placed to reduce the temperature gradient. The choice of this specific range of temperature was governed by our analytical capabilities (at temperatures below 300 °C, the solubility of gold is too low to be measurable using instrumental neutron activation analysis) and the critical temperature of water, for which the physical properties and behaviour are difficult to model. The vertical temperature gradient, measured with two chromel-alumel thermocouples located at the top and bottom of the aluminum box in the furnace, was typically less than 0.5 °C/m. A thermal regulator

allowed the temperature to be controlled to an accuracy of ± 1 °C. At the conditions of the experiments, water and liquid H₂S were converted entirely to gas. These gas mixtures, which varied in their proportions of H₂O and H₂S, filled the autoclaves and reacted with the solid in the holder. The amount of H₂O and H₂S placed in an autoclave was predetermined before the experiment ensuring that the system was liquid-undersaturated at the investigated conditions and gold dissolution occurred entirely in the dry vapour.

At the end of a set of experiments, the autoclaves were quenched to room temperature in a water bath and further cooled to a temperature of less than -70 °C in order to condense H₂S gas into liquid. The quartz-glass ampoules containing sulphur and gold were then removed from the autoclave and weighed to test for mass loss. Sulphur and gold precipitated on the walls of the autoclaves during the quenching were removed by washing with 1.5 to 3 ml of dilute (~10%) nitric acid at a temperature of 200 °C and 2 to 4 ml of freshly prepared aqua regia at room temperature (HNO₃ and HCl acids, Fisher Scientific OptimaTM grade). In order to ensure that no gold precipitates remained in the autoclaves, this washing procedure was repeated. The concentrations of gold in the washing solutions and hence dissolved in the H2O-H2S gas mixtures were determined using instrumental neutron activation analysis (INAA) at Ecole Polytechnique (University of Montreal) and ICP-MS (Geoscience Laboratories, Sudbury). The detection limit of the analytical technique was 0.1 µg/L and 0.05 ppb, respectively. The precision for INAA was $\pm 5\%$ for samples with concentrations greater than 1 µg/L Au and ± 0.05 µg/L for samples containing lower concentrations of Au. The amount of sulphur transferred to the gas phase was determined to an accuracy of ± 0.1 mg by weighing the ampoules loaded with sulphur before and after each run.

A series of blank experiments was undertaken in an atmosphere free of hydrogen sulphide (i.e., nitrogen gas) at each of the temperatures. The concentrations of Au in these runs were all below the detection limit of the analytical technique, indicating that there was no significant transport and precipitation of gold due simply to volatilization of the metal.

The attainment of equilibrium was tested with a series of kinetic experiments of varying duration (from 1 to 22 days) at the lowest temperature investigated (300 °C). Owing to the difficulty of maintaining the same pressure for a full set of kinetic runs (the pressure in each autoclave was slightly different due to small differences in the amount of H_2S introduced into them), the amount of transported Au was corrected to an arbitrarily chosen pressure of 100 bar. At a temperature of 300 °C, equilibrium was attained in less than 10 days; similar results were reported for kinetic experiments in a study of the solubility of Au in pure H_2S gas (Zezin et al., 2007). Subsequent experiments were conducted for longer durations (>12 days), thereby ensuring that the measured gold concentration represented the equilibrium concentration.

In order to test the hypothesis that mixed gold species containing sulphur and salts of alkali or alkali earth metals form in the presence of alkali or alkali earth metal chlorides (Zajacz et al., 2010), an additional set of experiments was carried out at 350 °C in which the autoclaves of holders containing sodium sulphide and chloride (Na₂S, anhydrous, and NaCl; both Alfa Aesar, 99.99% purity) were introduced. In other respects, these experiments duplicated those of Zezin et al. (2007), i.e., they were conducted in an atmosphere containing H₂S but not H₂O. Finally, a set of experiments involving only H₂O and gold was conducted for each of the temperatures investigated to test the hypothesis that gold solubility is enhanced by the formation of hydroxide species.

4.4. RESULTS

Experimental measurements of the solubility of gold in H_2O-H_2S gas mixtures were performed at temperatures of 300, 350 and 365 °C, and the mole fraction of H₂S in the gas mixture was varied from 0.03 to 0.96. The calculated pressure in the system was in the range 53 to 263 bar. The vapour pressure and fugacity coefficients were calculated from the measured temperature, volume and the masses of H₂O and H₂S introduced into the autoclave; the calculations were conducted using the equation of state of Peng and Robinson (1976) modified by Stryjek and Vera (1986). Partial pressures of gold species, as well as those of elemental sulphur and other sulphur species (except for H₂S) in the system were insignificant compared to the partial pressures of water and hydrogen sulphide. To our knowledge, information on the behaviour of reduced sulphur species in vapour other than that for H₂S at the temperatures of interest has not been published, and there are no experimental data that can be used to determine these pressures. Therefore, the total vapour pressure was assumed to be equal to that of pure H₂O-H₂S gas mixtures and only the binary system was considered in the calculations. Owing to the strongly nonideal behaviour of H₂O-H₂S fluid mixtures resulting from the dipolar nature of molecules of water and hydrogen sulphide, Margules-type composition-dependent mixing rules (Anderko, 2000) and system-specific binary interaction parameters were employed to facilitate the calculation of pressure and the fugacity coefficients of components in the

mixture (cf. Zezin et al., 2010). In contrast to H_2O and H_2S , the behaviour of gaseous gold and sulphur species was assumed to be ideal because of their very minor concentration in the gas phase compared to that of H_2O and H_2S . Accordingly, the partial pressures of Au and S were calculated from the ideal gas law, and the fugacities of Au and S species are considered equal to the corresponding partial pressures.

The results of the experimental measurements, the calculated pressures and the fugacities of components are presented in Table 4.1. The experiments were conducted in the vapour-only region. Consequently, the composition of the fluid was restricted to ensure that the H₂O-H₂S gas mixtures did not saturate with liquid at the temperature and pressure investigated (the equation of state and thermodynamic model developed by Zezin et al. (2010) were used to estimate the conditions at which the vapour becomes saturated with liquid). The detection limit of the analytical method (INAA) did not permit measurements of the solubility of gold at low pressure and concentration of H₂S (e.g., *P*< ~100 bar and $x_{H_2S(g)} < \sim 0.4$ at 300 °C).

The solubility of gold in H₂O-H₂S gas mixtures varied from 0.4 to 2.2 ppb at 300 °C, from 0.5 to 6.6 ppb at 350 °C and from 1.1 to 6.3 ppb at 365 °C. These raw data cannot be illustrated graphically in a meaningful way because of the dependence of the solubility of gold on the fugacity of both water and hydrogen sulphide. Thus, we present the data on diagrams showing the relationship between the log fugacity of gold and H₂S at nearly constant log f_{H_2O} (Fig. 4.1). For comparison, the calculated solubility of Au (log f_{Au}) in pure H₂S gas (Zezin et al., 2007) is also plotted in Figure 4.1. From this figure, it is evident that the addition of water vapour to H₂S gas only has a significant effect at a temperature above 300 °C and a fugacity of H₂O above ~ 20-40 bar. At these

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Р	V	ρ	H ₂ O	H_2S	y_{H_2S}	$\log f_{H_2S}$	$\log f_{H_2O}$	$\log f_{H_2}$	$\log f_{\sum Au}^{\mathrm{mod}}$	$\log f_{Au}^{\exp}$	Au
bar	cm ³	g/cm ³	mole	mole		bar	bar	bar	bar	bar	µg/kg
					30	0 °C					
95.3	36.1	0.062	0.056	0.036	0.39	1.50	1.66	-2.23	-8.27	-7.92	0.80
112.4	36.2	0.081	0.056	0.057	0.50	1.68	1.62	-2.06	-8.12	-7.88	0.67
59.0	37.0	0.043	0.006	0.044	0.88	1.69	0.75	-1.97	-8.31	-8.04	0.87
135.6	37.2	0.105	0.083	0.071	0.46	1.70	1.71	-2.06	-8.00	-7.75	0.70
134.8	37.8	0.104	0.083	0.072	0.46	1.70	1.71	-2.06	-8.01	-7.41	1.54
119.4	37.3	0.090	0.056	0.069	0.55	1.74	1.59	-1.99	-8.05	-7.95	0.52
67.0	36.2	0.050	0.006	0.050	0.89	1.75	0.74	-1.91	-8.21	-7.88	1.09
94.3	37.5	0.070	0.028	0.062	0.69	1.76	1.35	-1.93	-8.13	-7.97	0.64
125.5	36.0	0.097	0.056	0.073	0.57	1.77	1.59	-1.97	-8.01	-7.46	1.48
103.9	36.9	0.079	0.028	0.071	0.72	1.81	1.33	-1.88	-8.04	-7.83	0.77
153.5	37.4	0.130	0.083	0.099	0.54	1.82	1.66	-1.95	-7.88	-7.45	1.13
154.0	38.0	0.131	0.083	0.102	0.55	1.83	1.66	-1.94	-7.87	-7.48	1.05
83.2	36.8	0.064	0.006	0.066	0.92	1.84	0.69	-1.81	-8.05	-8.05	0.58
158.8	37.1	0.137	0.083	0.106	0.56	1.85	1.65	-1.93	-7.84	-7.17	2.04
140.4	36.2	0.115	0.056	0.093	0.62	1.86	1.55	-1.88	-7.89	-7.48	1.19
86.4	36.8	0.067	0.006	0.069	0.92	1.86	0.68	-1.79	-8.02	-7.74	1.13
159.9	37.9	0.139	0.083	0.111	0.57	1.86	1.64	-1.91	-7.83	-7.13	2.21
145.5	35.5	0.121	0.056	0.097	0.63	1.88	1.54	-1.87	-7.86	-7.38	1.42
145.5	35.8	0.121	0.056	0.098	0.64	1.88	1.54	-1.86	-7.86	-7.66	0.75
148.5	35.8	0.125	0.056	0.102	0.65	1.89	1.53	-1.85	-7.83	-7.80	0.52
95.4	37.0	0.075	0.006	0.078	0.93	1.90	0.66	-1.75	-7.95	-8.04	0.51
122.7	36.6	0.098	0.028	0.091	0.76	1.91	1.29	-1.79	-7.89	-7.95	0.47
127.1	36.9	0.103	0.028	0.097	0.78	1.93	1.27	-1.77	-7.85	-7.60	1.01
181.6	37.9	0.169	0.083	0.145	0.64	1.96	1.58	-1.83	-7.68	-7.39	0.99

Table 4.1. Measured and calculated experimental data and results of modeling.

Р	V	ρ	H ₂ O	H_2S	y_{H_2S}	$\log f_{H_2S}$	$\log f_{H_2O}$	$\log f_{H_2}$	$\log f_{\sum Au}^{\mathrm{mod}}$	$\log f_{Au}^{\exp}$	Au
bar	cm ³	g/cm ³	mole	mole		bar	bar	bar	bar	bar	µg/kg
113.2	36.2	0.091	0.006	0.093	0.94	1.98	0.62	-1.68	-7.82	-7.66	1.00
143.5	37.1	0.120	0.028	0.116	0.81	1.99	1.22	-1.71	-7.74	-7.75	0.61
124.4	36.5	0.101	0.006	0.105	0.95	2.02	0.59	-1.64	-7.75	-7.91	0.50
179.7	36.0	0.164	0.056	0.144	0.72	2.02	1.45	-1.75	-7.63	-7.73	0.47
200.3	37.4	0.195	0.083	0.171	0.67	2.02	1.54	-1.78	-7.57	-7.41	0.82
183.8	35.7	0.169	0.056	0.148	0.73	2.03	1.44	-1.74	-7.60	-7.44	0.89
157.9	37.4	0.135	0.028	0.134	0.83	2.04	1.18	-1.67	-7.65	-7.30	1.53
159.6	37.9	0.137	0.028	0.138	0.83	2.05	1.17	-1.67	-7.64	-7.63	0.71
201.4	36.0	0.191	0.056	0.172	0.75	2.08	1.39	-1.70	-7.50	-7.66	0.47
158.9	36.9	0.133	0.006	0.141	0.96	2.12	0.50	-1.57	-7.56	-7.75	0.55
206.1	37.4	0.187	0.028	0.19	0.87	2.17	1.06	-1.60	-7.39	-7.73	0.41
					350	0 °C					
169.4	37.5	0.114	0.222	0.008	0.03	0.63	2.05	-3.02	-6.92	-6.77	5.67
172.9	35.9	0.122	0.222	0.011	0.05	0.83	2.05	-2.82	-6.92	-6.75	5.56
174.8	35.2	0.126	0.222	0.013	0.06	0.85	2.05	-2.80	-6.93	-6.91	3.71
171.7	37.7	0.119	0.222	0.015	0.06	0.91	2.04	-2.74	-6.95	-7.21	1.96
142.5	36.3	0.081	0.139	0.013	0.09	0.98	1.98	-2.64	-7.10	-7.33	2.19
170.3	34.5	0.117	0.194	0.016	0.08	0.99	2.03	-2.65	-6.97	-7.24	1.87
102.1	37.1	0.050	0.083	0.011	0.12	1.01	1.86	-2.60	-7.38	-7.64	1.73
175.8	37.5	0.128	0.222	0.024	0.10	1.12	2.03	-2.52	-6.98	-6.81	4.59
177.7	36.3	0.133	0.222	0.024	0.10	1.12	2.03	-2.52	-6.97	-6.79	4.65
145.9	36.2	0.086	0.139	0.018	0.11	1.13	1.97	-2.50	-7.12	-7.20	2.79
177.1	36.9	0.131	0.222	0.025	0.10	1.14	2.03	-2.50	-6.98	-6.81	4.49
149.0	35.2	0.089	0.139	0.019	0.12	1.16	1.98	-2.47	-7.11	-7.11	3.30
147.2	36.3	0.088	0.139	0.02	0.13	1.17	1.97	-2.45	-7.12	-7.10	3.44

Table 4.1. (continued)

Р	V	ρ	H ₂ O	H_2S	y_{H_2S}	$\log f_{H_2S}$	$\log f_{H_2O}$	$\log f_{H_2}$	$\log f_{\sum Au}^{\mathrm{mod}}$	$\log f_{Au}^{\exp}$	Au
bar	cm ³	g/cm ³	mole	mole		bar	bar	bar	bar	bar	µg/kg
177.3	37.4	0.131	0.222	0.027	0.11	1.17	2.02	-2.47	-6.98	-6.93	3.40
177.7	37.2	0.132	0.222	0.027	0.11	1.17	2.02	-2.47	-6.98	-6.88	3.79
151.1	37.6	0.093	0.148	0.024	0.14	1.23	1.97	-2.39	-7.12	-7.11	3.19
175.4	35.0	0.127	0.194	0.028	0.13	1.24	2.01	-2.40	-7.01	-6.73	5.57
147.4	37.4	0.089	0.139	0.024	0.15	1.25	1.96	-2.37	-7.15	-6.81	6.63
162.3	37.5	0.106	0.167	0.029	0.15	1.29	1.98	-2.34	-7.09	-7.50	1.13
150.1	37.4	0.092	0.139	0.028	0.17	1.32	1.95	-2.30	-7.16	-7.44	1.49
114.1	36.5	0.062	0.083	0.023	0.22	1.33	1.84	-2.26	-7.41	-7.37	2.60
59.1	36.2	0.031	0.028	0.018	0.39	1.34	1.50	-2.24	-8.04	-7.70	2.46
150.7	37.7	0.093	0.139	0.03	0.18	1.34	1.95	-2.27	-7.17	-7.19	2.63
91.4	35.8	0.048	0.056	0.021	0.27	1.35	1.74	-2.24	-7.62	-7.94	0.91
185.4	37.4	0.147	0.222	0.044	0.17	1.39	2.00	-2.24	-7.03	-6.91	3.19
154.0	37.5	0.098	0.139	0.034	0.20	1.40	1.94	-2.21	-7.18	-7.58	1.02
160.7	35.3	0.106	0.139	0.036	0.21	1.44	1.95	-2.18	-7.16	-7.43	1.34
156.5	37.6	0.101	0.139	0.038	0.21	1.45	1.93	-2.16	-7.19	-7.43	1.40
140.3	37.5	0.085	0.111	0.035	0.24	1.46	1.89	-2.14	-7.29	-7.24	2.57
158.2	37.5	0.103	0.139	0.04	0.22	1.47	1.93	-2.14	-7.19	-6.96	4.04
188.8	34.2	0.151	0.194	0.049	0.20	1.50	1.98	-2.13	-7.06	-6.73	4.69
143.7	37.4	0.089	0.111	0.039	0.26	1.51	1.88	-2.09	-7.29	-7.13	3.17
145.8	37.4	0.091	0.112	0.041	0.27	1.53	1.88	-2.07	-7.29	-7.58	1.10
191.8	34.3	0.156	0.194	0.054	0.22	1.54	1.97	-2.09	-7.07	-6.75	4.35
73.0	35.8	0.042	0.028	0.029	0.51	1.54	1.48	-2.02	-7.90	-7.68	1.90
196.6	37.2	0.166	0.222	0.064	0.22	1.57	1.97	-2.06	-7.07	-6.74	4.17
168.2	36.9	0.116	0.139	0.052	0.27	1.59	1.92	-2.01	-7.20	-7.43	1.22
169.7	37.2	0.118	0.139	0.055	0.28	1.61	1.91	-1.99	-7.21	-7.43	1.20

Table 4.1. (continued)

Р	V	ρ	H ₂ O	H_2S	y_{H_2S}	$\log f_{H_2S}$	$\log f_{H_2O}$	$\log f_{H_2}$	$\log f_{\sum Au}^{\mathrm{mod}}$	$\log f_{Au}^{\exp}$	Au
bar	cm ³	g/cm ³	mole	mole		bar	bar	bar	bar	bar	µg/kg
200.9	37.4	0.172	0.222	0.072	0.24	1.62	1.96	-2.01	-7.08	-7.12	1.67
154.7	37.2	0.101	0.111	0.052	0.32	1.63	1.86	-1.96	-7.30	-7.52	1.13
199.5	34.3	0.167	0.194	0.066	0.25	1.63	1.96	-1.99	-7.09	-7.16	1.57
113.5	35.8	0.068	0.056	0.042	0.43	1.65	1.70	-1.92	-7.58	-7.28	2.93
172.8	37.4	0.122	0.139	0.06	0.30	1.65	1.90	-1.95	-7.22	-7.13	2.32
174.7	38.1	0.124	0.139	0.065	0.32	1.68	1.89	-1.92	-7.23	-7.76	0.53
85.9	37.1	0.052	0.028	0.042	0.60	1.68	1.45	-1.87	-7.78	-7.56	2.01
177.7	37.5	0.127	0.139	0.067	0.33	1.70	1.89	-1.90	-7.22	-7.10	2.37
144.1	36.0	0.093	0.083	0.054	0.39	1.70	1.79	-1.87	-7.40	-7.63	0.96
167.6	34.7	0.115	0.111	0.059	0.35	1.70	1.86	-1.88	-7.27	-6.78	5.47
143.4	36.6	0.092	0.083	0.055	0.40	1.71	1.79	-1.87	-7.41	-7.16	2.86
184.1	37.5	0.135	0.139	0.075	0.35	1.75	1.88	-1.85	-7.22	-7.14	2.04
66.6	37.3	0.044	0.006	0.045	0.88	1.75	0.82	-1.79	-7.79	-7.74	1.57
175.4	34.8	0.124	0.111	0.068	0.38	1.77	1.85	-1.82	-7.27	-7.41	1.19
99.4	36.2	0.063	0.028	0.052	0.65	1.78	1.43	-1.76	-7.67	-7.93	0.71
201.8	37.5	0.160	0.167	0.088	0.35	1.78	1.90	-1.83	-7.16	-7.10	1.88
105.5	37.0	0.068	0.028	0.059	0.68	1.82	1.42	-1.71	-7.62	-7.73	1.04
161.5	37.1	0.110	0.083	0.076	0.48	1.84	1.75	-1.72	-7.36	-7.07	2.94
162.6	37.1	0.111	0.083	0.077	0.48	1.84	1.75	-1.72	-7.36	-7.64	0.78
199.6	37.5	0.153	0.139	0.095	0.41	1.85	1.85	-1.74	-7.20	-7.03	2.32
170.9	36.2	0.119	0.083	0.083	0.50	1.88	1.74	-1.68	-7.33	-7.26	1.75
206.8	37.6	0.161	0.139	0.104	0.43	1.89	1.84	-1.70	-7.19	-7.39	0.96
209.6	37.5	0.164	0.139	0.107	0.43	1.90	1.84	-1.69	-7.19	-7.09	1.88
213.1	37.2	0.168	0.139	0.11	0.44	1.92	1.83	-1.67	-7.18	-6.92	2.72
176.9	37.5	0.125	0.083	0.094	0.53	1.92	1.72	-1.63	-7.31	-7.52	0.92

Table 4.1. (continued)

Р	V	ρ	H ₂ O	H_2S	y_{H_2S}	$\log f_{H_2S}$	$\log f_{H_2O}$	$\log f_{H_2}$	$\log f_{\sum Au}^{\mathrm{mod}}$	$\log f_{Au}^{\exp}$	Au
bar	cm ³	g/cm ³	mole	mole		bar	bar	bar	bar	bar	µg/kg
131.7	35.2	0.089	0.028	0.077	0.73	1.95	1.40	-1.56	-7.46	-7.55	1.20
103.1	36.9	0.071	0.006	0.074	0.93	1.95	0.78	-1.54	-7.50	-7.44	1.94
132.8	35.5	0.090	0.028	0.079	0.74	1.95	1.40	-1.56	-7.45	-7.57	1.14
234.5	37.4	0.191	0.139	0.136	0.49	2.01	1.80	-1.58	-7.12	-7.00	1.99
150.1	36.8	0.104	0.028	0.098	0.78	2.02	1.36	-1.47	-7.36	-7.56	1.00
124.6	37.0	0.088	0.006	0.092	0.94	2.03	0.75	-1.44	-7.38	-7.53	1.28
161.2	37.1	0.114	0.028	0.109	0.80	2.06	1.34	-1.42	-7.30	-7.39	1.36
137.3	36.7	0.098	0.006	0.102	0.94	2.07	0.74	-1.39	-7.32	-7.53	1.15
198.8	36.1	0.145	0.056	0.124	0.69	2.08	1.57	-1.43	-7.21	-7.42	1.00
169.5	35.6	0.120	0.028	0.111	0.80	2.08	1.35	-1.40	-7.27	-7.29	1.62
263.1	37.8	0.219	0.139	0.169	0.55	2.10	1.77	-1.49	-7.04	-6.88	2.29
187.8	35.6	0.136	0.028	0.127	0.82	2.13	1.32	-1.34	-7.20	-7.47	0.95
176.0	37.1	0.128	0.006	0.136	0.96	2.17	0.69	-1.26	-7.18	-7.44	1.08
					365	5 °C					
171.3	37.5	0.102	0.194	0.009	0.05	0.74	2.06	-2.85	-6.87	-7.17	2.46
76.5	35.9	0.033	0.056	0.005	0.09	0.77	1.78	-2.81	-7.51	-7.60	2.83
174.4	36.4	0.106	0.194	0.011	0.05	0.82	2.06	-2.77	-6.87	-7.02	3.33
129.5	36.2	0.065	0.111	0.011	0.09	0.96	1.96	-2.62	-7.10	-7.35	2.54
179.4	36.0	0.116	0.194	0.020	0.09	1.10	2.05	-2.49	-6.90	-7.05	2.85
201.2	37.2	0.163	0.278	0.030	0.10	1.17	2.07	-2.42	-6.86	-6.67	4.88
180.7	36.3	0.119	0.194	0.024	0.11	1.17	2.04	-2.41	-6.92	-6.84	4.52
53.5	37.5	0.026	0.028	0.014	0.33	1.23	1.51	-2.33	-7.96	-7.74	2.61
136.7	36.7	0.074	0.111	0.021	0.16	1.26	1.94	-2.31	-7.14	-7.43	1.86
181.4	37.3	0.120	0.194	0.029	0.13	1.27	2.03	-2.31	-6.94	-7.01	3.01
204.2	37.4	0.169	0.278	0.039	0.12	1.29	2.06	-2.29	-6.88	-6.72	4.18

Table 4.1. (continued)

Р	V	ρ	H ₂ O	H_2S	y_{H_2S}	$\log f_{H_2S}$	$\log f_{H_2O}$	$\log f_{H_2}$	$\log f_{\sum Au}^{\mathrm{mod}}$	$\log f_{Au}^{\exp}$	Au
bar	cm ³	g/cm ³	mole	mole		bar	bar	bar	bar	bar	µg/kg
140.7	36.2	0.078	0.111	0.024	0.18	1.33	1.94	-2.23	-7.15	-7.35	2.12
210.6	37.0	0.182	0.278	0.052	0.16	1.43	2.04	-2.14	-6.91	-6.65	4.56
144.1	37.5	0.083	0.111	0.032	0.23	1.45	1.91	-2.10	-7.18	-7.32	2.15
192.7	36.2	0.138	0.194	0.044	0.18	1.47	2.01	-2.09	-6.98	-6.77	4.57
192.7	36.2	0.138	0.194	0.044	0.18	1.47	2.01	-2.09	-6.98	-7.09	2.19
148.1	36.2	0.086	0.111	0.033	0.23	1.47	1.92	-2.08	-7.16	-7.46	1.49
146.3	37.4	0.085	0.111	0.035	0.24	1.48	1.91	-2.07	-7.18	-7.52	1.32
100.0	36.3	0.053	0.056	0.027	0.33	1.49	1.73	-2.06	-7.48	-7.21	4.30
198.9	35.8	0.147	0.194	0.052	0.21	1.55	2.00	-2.00	-6.99	-6.60	6.34
153.8	36.2	0.092	0.111	0.040	0.26	1.55	1.91	-1.99	-7.17	-6.94	4.61
219.7	37.4	0.196	0.278	0.069	0.20	1.57	2.02	-1.98	-6.95	-6.83	2.80
224.0	37.2	0.203	0.278	0.075	0.21	1.62	2.02	-1.93	-6.95	-6.67	3.91
226.8	37.0	0.208	0.278	0.079	0.22	1.65	2.01	-1.90	-6.96	-6.79	2.90
165.6	35.8	0.104	0.111	0.051	0.32	1.67	1.89	-1.86	-7.15	-7.05	3.17
164.7	36.3	0.104	0.111	0.052	0.32	1.67	1.89	-1.86	-7.16	-7.06	3.12
122.9	36.0	0.072	0.056	0.047	0.46	1.72	1.70	-1.80	-7.35	-7.67	1.10
237.7	37.5	0.220	0.278	0.095	0.25	1.74	1.99	-1.79	-6.97	-6.99	1.73
179.1	35.8	0.118	0.111	0.065	0.37	1.78	1.87	-1.73	-7.12	-7.42	1.20
225.7	36.5	0.179	0.194	0.089	0.31	1.81	1.95	-1.70	-7.00	-6.98	2.17
107.4	37.3	0.066	0.028	0.057	0.67	1.83	1.44	-1.66	-7.33	-7.47	1.91
201.9	35.2	0.140	0.111	0.085	0.43	1.91	1.84	-1.58	-7.05	-6.94	3.05
250.8	37.1	0.204	0.194	0.119	0.38	1.95	1.91	-1.54	-6.95	-6.79	2.96
207.8	37.5	0.144	0.111	0.100	0.47	1.96	1.82	-1.52	-7.02	-7.05	2.29
142.3	37.6	0.092	0.028	0.087	0.76	2.00	1.40	-1.46	-7.09	-7.04	3.66
223.1	35.7	0.159	0.111	0.107	0.49	2.01	1.81	-1.46	-6.97	-6.57	6.30

Table 4.1. (continued)

Р	V	ρ	$\mathrm{H}_{2}\mathrm{O}$	$\mathrm{H}_2\mathrm{S}$	\mathcal{Y}_{H_2S}	$\log f_{H_2S}$	$\log f_{H_2O}$	$\log f_{H_2}$	$\log f_{\sum Au}^{\mathrm{mod}}$	$\log f_{Au}^{\exp}$	Au
bar	cm ³	g/cm ³	mole	mole		bar	bar	bar	bar	bar	µg/kg
232.1	35.8	0.167	0.111	0.116	0.51	2.04	1.80	-1.37	-6.93	-6.79	4.56
196.2	37.0	0.132	0.056	0.114	0.67	2.08	1.61	-1.29	-6.80	-6.82	4.11
253.4	34.7	0.186	0.111	0.130	0.54	2.10	1.79	-2.85	-6.87	-7.17	2.46
200.1	36.2	0.137	0.028	0.131	0.82	2.17	1.37	-2.81	-7.51	-7.60	2.83

Table 4.1. (continued)

P – pressure, V – volume, ρ – density, y_{H_2S} – mole fraction of H₂S in vapour

Figure 4.1. Plots of $\log f_{Au}$ vs. $\log f_{H_2S}$ for 300 °C (a, b, c), 350 °C (d, e, f) and 365 °C (g, h, i) at three intervals of f_{H_2O} . The filled symbols represent the experimental data and the open symbols calculated values based on equilibrium constants determined for reactions 5 and 6. The dotted line indicates the solubility of Au in pure H₂S determined by Zezin et al. (2007). The error bar represents the standard deviation of the experimentally-determined fugacity of gold from that calculated (0.20 at 300 °C, 0.21 at 350 °C, 0.21 at 365 °C). See text for further details.



conditions, the solubility of Au increases with increasing fugacity of water, suggesting that complexes of gold with hydrogen sulphide contribute to the dissolution of gold by H₂S-bearing vapour (Fig. 4.1 b, e, h). At high fugacity of H₂O, the solubility of Au is controlled by complexes containing only H₂O (Fig 4.1 c, f, i); the fluctuations in the observed solubility at these conditions are due to small variations in f_{H_2O} , as well as variations in the activity of elemental sulphur required to control the redox conditions.

In the experiments with pure H_2O vapour, which were conducted at variable pressure, the concentration of gold dissolved in vapour was below the detection limit. Thus, we conclude that formation of hydroxide or other sulphur-free gold species in the vapour has a negligible influence on the dissolution of the gold. The experiments with sodium sulphide, sodium chloride and H_2S but not H_2O yielded results indistinguishable from those with only hydrogen sulphide (Zezin et al.; 2007; see 4.1 d), indicating that formation of mixed polymetallic complexes with alkali earth metals is insignificant and does not affect the dissolution of gold at the conditions considered in this study.

4.5. DISCUSSION

4.5.1. Stability and Stoichiometry of Au Species in H₂O-H₂S Gas Mixtures

The experimental data were treated using a hydration or solvation model, which has been discussed in considerable detail in previous publications on the solubility and complexation of a solid in the gas phase or water vapour (e.g., Migdisov et al., 1999; Archibald et al., 2001; Archibald et al., 2002; Zakaznova-Iakovleva et al., 2001;

Migdisov and Williams-Jones, 2005; Rempel et al., 2006 and 2008; Zezin et al., 2007). The solubility of Au in H_2O-H_2S gas mixtures is believed to be due to complexation with sulphur and solvation. Thus, the concentrations of gold measured in the experiments are interpreted to reflect the following reactions:

$$Au(s) + (n+1)H_2S(g) = AuS \cdot (H_2S)_n(g) + H_2(g)$$
(2)

$$Au(s) + H_2S(g) + mH_2O(g) = AuS \cdot (H_2O)_m(g) + H_2(g)$$
(3)

where *n* is the solvation number and *m* is the hydration number of the gold species or the number of H_2S or H_2O molecules in the first shell adjacent to a gold-bearing species and held there by van der Waals bonding. It is important to note that by combining the above reactions with the reaction buffering the fugacity of hydrogen in the experiments, i.e.

$$S(l) + H_2(g) = H_2 S(g) , (4)$$

equilibrium in the experimental system can also be described by the following pair of reactions:

$$Au(s) + S(l) + nH_2S(g) = AuS \cdot (H_2S)_n(g)$$
⁽⁵⁾

$$Au(s) + S(l) + mH_2O(g) = AuS \cdot (H_2O)_m(g)$$
(6)

The equilibrium constants of these reactions were evaluated from the general thermodynamic relations:

$$\log K_{5} = \log f_{AuS \cdot (H_{2}S)_{n}(g)} - n \cdot \log f_{H_{2}S(g)} - \log a_{S(l)}$$
(7)

$$\log K_{6} = \log f_{AuS \cdot (H_{2}O)_{m}(g)} - m \cdot \log f_{H_{2}O(g)} - \log a_{S(l)}$$
(8)

As discussed by Zezin et al. (2007), it is also equally possible that instead of occurring as the sulphide molecule, AuS, the gold occurs as the bisulphide molecule, AuHS, or that both species are present in the gas mixture. The experimental method employed in this

study is not designed to distinguish between these two molecules, but statistically (see discussion below), the formation of a sulphide species is favoured. Therefore, calculation of the solubility of gold in the vapour will assume that the gold is present in the form of solvated AuS molecules.

The elemental sulphur used in the experiments to control the fugacity of hydrogen (see equation 4) is a liquid at the investigated conditions. As H₂S dissolves in liquid sulphur, the activity of sulphur was not equal to unity and was therefore calculated in order to derive the equilibrium constants of the gold dissolution reactions using equations 7 and 8. From the known activity of liquid sulphur and the fugacity of H₂S, it was also possible to calculate values of f_{H_2} in the experiments, thereby allowing the equilibrium constants of the reactions 2 and 3) to be determined.

The activity of sulphur in the melt was estimated in a manner similar to that described by Zezin et al. (2007). This involved mass balance calculations that take into account the reactions between liquid sulphur and a variety of gaseous sulphur species, S_i (with *i* ranging from 2 to 8), as well as reactions for the formation of hydrogen polysulphide species H_2S_i (where *j* varies from 2 to 6):

$$iS(l) = S_i(g) , K_{S_i} = \frac{f_{S_i(g)}}{a_{S(l)}^i}$$
(9)

$$H_2S(g) + (j-l)S(l) = H_2S_j(g) , K_{H_2S_j} = \frac{f_{H_2S_j(g)}}{f_{H_2S(g)} \cdot a_{S(l)}^{j-l}}$$
(10)

Assuming that the fugacities of gaseous S_i and H_2S_j are equal to their partial pressures, we can calculate the activity of S(l) by comparing the total partial pressure of components participating in reactions involving sulphur to the pressure calculated from the

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experimental measurements of sulphur losses to the vapour from the ampoule containing liquid:

$$P_{S}^{\exp} = \sum_{i=1}^{8} \left(i \cdot P_{S_{i}(g)} \right) + \sum_{j=2}^{6} P_{H_{2}S_{j}(g)} = \sum_{i=1}^{8} \left(i \cdot K_{S_{i}} \cdot (a_{S(l)})^{i} \right) + \sum_{j=2}^{6} \left(K_{H_{2}S_{j}} \cdot f_{H_{2}S(g)} \cdot (a_{S(l)})^{j-1} \right)$$
(11)

The values of the equilibrium constants K_{S_i} and $K_{H_2S_j}$, which are both T- and Pdependent constants, were calculated from the thermodynamic data of Mills (1974) and Suleimenov and Ha (1998), and the value for $f_{H,S}$ from the equation of state for H₂O-H₂S gas mixtures (Zezin et al., 2010). The total partial pressure of sulphur species was determined from the experimental data using the ideal gas law, $P_S^{exp} = \frac{N_S RT}{V}$, where N_S is the number of moles of sulphur lost from the ampoule during an experiment, R is the gas constant, T is the temperature, and V is the volume of the autoclave after subtraction of the volumes of gold- and sulphur-containing ampoules. Figure 4.2 shows the dependence of the partial pressure of sulphur in the experiments (P_S^{exp}) on the total vapour pressure in the H₂O-H₂S gas mixture. These pressures are remarkably similar to the pressures of sulphur obtained in experiments with pure H₂S by Zezin et al. (2007). As can be seen from reaction 11, the partial pressure of hydrogen polysulphide species, H_2S_i , is dependent on the fugacity of hydrogen sulphide in the gas mixture, which, in turn, is a function of total pressure and the mole fraction of H₂S. This additional compositional dependence can explain the spread in data for the measured solubility of sulphur in the experiments with H_2O-H_2S mixtures compared to those with pure H_2S gas (open and filled symbols in Figure 4.2). The activity of liquid sulphur calculated at each temperature from the experimentally-determined total partial pressure of sulphur species and partial



Figure 4.2. The solubility of sulphur in H₂O-H₂S gas mixtures (open diamonds; this study) and pure H₂S gas (filled squares; Zezin et al., 2007) presented as total partial pressures of the gaseous sulphur species (S_i and H₂S_j). (a) 300 °C, (b) 350 °C and (c) 365 °C.

pressures of S_i and H_2S_j gas species calculated from the thermodynamic data were approximated by a simple polynomial function of total pressure and the composition of the gas mixture (Table 4.2). The standard deviations obtained using this function are less than 0.14, 0.05 and 0.2 units at temperatures of 300, 350 and 365 °C, respectively.

As H₂S gas was present in all the experiments, the gold dissolved partly via formation of gaseous sulphide complexes solvated by H₂S, i.e. $AuS \cdot (H_2S)_n$. The contribution of these solvated species to the total solubility of Au in the H₂O-H₂S gas mixtures was assessed using the equilibrium constants for reaction 5 and the corresponding solvation numbers (*n*) given by Zezin et al. (2007). These values vary with temperature and were therefore interpolated in order to obtain the equilibrium constant and the solvation number at 365 °C.

Further interpretation of the experimental data was carried out using a customdesigned optimization algorithm in the Matlab[®] software package. The hydration number m of the gold sulphide molecule, $AuS \cdot (H_2O)_m$, was adjusted together with the equilibrium constants of reaction 6 in order to minimize the difference between the logarithms of the fugacity of Au calculated from the experimental measurements, $\log f_{Au}^{exp}$, and the sum of the partial pressures of gold species, i.e., "cumulative" fugacity, $\log f_{\Delta u}^{mod}$, (based on the assumption of ideal behaviour). The latter was calculated from the thermodynamic relations describing the equilibrium dissolution of Au in H₂O-H₂S gas mixtures based on solvation of gold species by H₂S and their hydration by H₂O (reactions 5 and 6 and corresponding equations 7 and 8). The objective function of the optimization algorithm is represented by the following expression:

Table 4.2. Coefficients for the polynomial equation employed to estimate the activity of liquid sulphur $(a_{S(l)})$ in the presence of a H₂O-H₂S gas mixture.

	$a_{\mathrm{S}(\mathrm{l})}$	$= a + b \cdot P +$	$\mathbf{c} \cdot P^2 + \mathbf{d} \cdot x_H$	$H_{2S(g)} + e \cdot P \cdot x_{P}$	$H_2S(g)$	st.dev.
<i>T</i> °C	a	b·10 ⁴	c·10 ⁶	$d \cdot 10^2$	$e \cdot 10^3$	
300	0.7483	1.898	9.763	-5.124	-2.163	±0.14
350	0.9765	-9.040	6.708	-2.437	-2.356	±0.05
365	1.1091	-13.72	4.631	-4.556	-2.311	±0.02

$$U = 100\% \cdot \frac{1}{N} \sum \left(\frac{\log f_{Au}^{\exp} - \log f_{\Delta u}^{\text{mod}}}{\log f_{Au}^{\exp}} \right)^2$$
(12)

The equilibrium constants (K_6) and the hydration numbers (m) of reaction 6 were calculated for each isothermal data set independently. The results of the optimization (K_6 , m) and the set of equilibrium constants for the H₂S solvation reaction (reaction 5; K_5) and the solvation numbers (n) given by Zezin et al. (2007) are presented in Table 4.3. The equilibrium constants for reaction 3 were calculated from the parameters derived for reaction 6 (K_6 , m) and equilibrium constants for reaction 4 (the latter were obtained from the thermodynamic database contained in the *HCh* computer package; Shvarov and Bastrakov, 1999). The error limits reported in Table 4.3 were calculated in the manner described by Migdisov et al. (2006). As in case of the experiments conducted in pure H₂S gas, the error propagated from the experimental uncertainties and errors associated with the calculations of the fugacity of components from the equation of state and activity of sulphur are significantly less than the reported error limits related to the optimization procedure described above (e.g., propagated errors on log K values are 0.13, 0.05 and 0.18 at temperatures 300, 350 and 365 °C, respectively). The distribution of the error limits was modeled as a function of the guessed equilibrium constant and hydration number for reaction 6. The total mean error was calculated using equation 12. Sliced profiles of these error surfaces at constant values of the hydration number revealed an asymmetrical distribution (see example for the 350 °C isotherm in Figure 4.3; the error distribution has the same pattern for the other temperatures). The horizontal line in Figure 4.3 represents the accuracy of the experimental method ε_{max} calculated for the largest deviation of the modeled fugacity of gold (using equations 7 and 8) from that determined

Table 4.3. Equilibrium constants and H₂S-solvation/hydration numbers for the reactions controlling the formation of $AuS \cdot (H_2S)_n(g)$ - reactions 2 and 5, and $AuS \cdot (H_2O)_m(g)$ - reactions 3 and 6.

	$AuS \cdot$	$(H_2S)_n(g)$		$AuS \cdot (H_2O)_m(g)$							
T °C	$\log K_2^*$	$\log K_5^*$	n [*]	$\log K_3^{**}$	$\log K_6$	(error)	т	(error)			
300	-14.9	-11.1	1.8	-15.3	-11.4	(+0.5/-1.2)	2.3	(+0.3/-0.8)			
350	-14.4	-10.7	1.7	-15.3	-11.6	(+0.6/-0.7)	2.3	(+0.3/-0.3)			
365	-14.2	-10.6	1.8	-15.1	-11.6	(+0.5/-0.6)	2.2	(+0.3/-0.3)			

- data from Zezin et al. (2007); values at 365 °C are interpolations from data at 350 and 400 °C.

** - calculated from the optimized values of log K_6 and m and equilibrium constants for reaction $H_2+S=H_2S$.



Figure 4.3. Profiles of the distribution of the total error associated with the fit for the equilibrium constant and hydration number for reaction 6 at 350 °C. (a) The dependence of the total error on the assumed hydration number at a fixed value of the equilibrium constant. (b) The dependence of the total error on the assumed equilibrium constant at a fixed value of the hydration number. The gray area represents the region for which derivation of the parameters, K_6 and m, requires an accuracy higher than is possible with the experimental method.

experimentally according to the following relation:

$$\varepsilon_{\max} = 100\% \cdot \left(\frac{\log f_{Au}^{\exp} - \log f_{\sum Au}^{\mod}}{\log f_{Au}^{\exp}}\right)^2$$
(13)

The optimized values of the logarithm of the equilibrium constant and hydration number for reaction 6 correspond to the minimum for the error distribution in Figures 4.3a and 4.3b, respectively. The errors of the optimized parameters (K_6 and m) were determined from the intersection of the distribution profile with the horizontal line representing the accuracy of the experimental method. The estimates of the goodness of fit are also presented in Figure 4.1, as error bars. They are represented by standard deviations of the calculated fugacity of Au in the experiments from that calculated using equations 7 and 8 based on the adjusted equilibrium constant and hydration number; the corresponding values at temperatures of 300, 350 and 365 °C are 0.20, 0.21 and 0.21 log units.

From the results of the optimization and statistical tests, it would appear that the dominant hydrated species of gold in vapour is a sulphide, i.e., $AuS \cdot (H_2O)_m$. The optimization algorithm was not able to return meaningful and consistent results for gold bisulphide, $AuHS \cdot (H_2O)_m$. In particular, the hydration number increases from 2 to 3 over the relatively small temperature interval from 300 to 350 °C, which seems unreasonable. Furthermore, the standard deviations for the calculated solubility of gold from the experimental values at all temperatures are significantly higher for the bisulphide species than for the sulphide species. These findings are supported by spectrometric analyses of the speciation of gaseous molecules of gold (Gingerich, 1970) and other metals (e.g., As, Sb, Cd, Pb; see Palatnik et al., 1970; Sullivan, 1970; Botor et al., 1989; Hino et al., 1986), which consistently show that the metallic gas species is a

sulphide rather than a bisulphide complex. In summary, we therefore conclude that the solubility of gold in H_2O-H_2S gas mixtures is governed by the stability of solvated/hydrated gold sulphide species.

4.5.2. Distribution of Au Species

Using the optimized values of the formation constants for reactions 5 and 6 and hydration numbers for sulphide complexes, it is now possible to model the distribution of Au species in H₂O-H₂S gas mixtures. Figure 4.4 shows predominance diagrams for these species at 300, 350 and 365 °C for a fugacity of H₂S of 10 bar (Fig. 4.3a) and at 350 °C for a fugacity of H₂S of 10, 50 and 200 bar (Fig. 4.3b), based on this modeling.

The measured solubility (or the fugacity of dissolved gold species) for experiments involving mixtures of H₂O and H₂S gases defines the same trends as those observed for experiments involving pure H₂S gas at a fugacity of H₂O below ~20-40 bar (Fig. 4.1 a, d, g). As there is no significant increase in the solubility of gold with the addition of water to the system at or below this fugacity of H₂O, and there is a positive correlation of log f_{Au}^{exp} with log f_{H_2S} , we conclude that reaction 5 dominates and controls the solubility of gold at these conditions. At greater values of f_{H_2O} , however, the solubility of Au in the vapour increases progressively (Fig.4.1 and Fig. 4.3) indicating the contribution of a hydrated species of gold, such as $AuS \cdot (H_2O)_m$.

It is important to note that, although the solubility of Au is largely determined by hydrated species at high fugacity of H_2O , i.e., the conditions encountered in natural hydrothermal fluids, the presence of H_2S is essential to ensure the formation of gold

Figure 4.4. The modeled log fugacity of Au as a function of $\log f_{H_2O}$ in H₂O-H₂S gas mixtures. (a) The log fugacity of Au at 300, 350 and 365 °C and constant fugacity of H₂S (10 bar). The light horizontal lines show the log fugacity of Au as the species $AuS \cdot (H_2S)_n$, the light inclined lines its log fugacity as the species $AuS \cdot (H_2O)_m$ and the heavy lines the sum of the contributions of the two species $(\log f_{\Delta u}^{mod})$, i.e., the logarithm of the total partial pressure of Au or "cumulative" fugacity. The species $AuS \cdot (H_2O)_m$ becomes predominant at values of $\log f_{H_2O}$ ranging from above 0.9 at 350 °C to above 1.25 at 365 °C. (b) The log fugacity of Au at 350 °C and a fugacity of H₂S ranging from 10 to 200 bar (see caption to (a) and main text for further details).



sulphide molecules. Without this molecule or a gold molecule involving another suitable ligand, the solubility of Au would be negligible, as was shown earlier for experiments with pure H₂O. It is evident from our experiments that hydrogen sulphide is the source of the reduced sulphur involved in the dissolution of gold (reaction 3). As this reaction is redox-sensitive and the S/H₂S buffer pair was used to constrain f_{H_2} in our experiments, it was convenient to perform calculations based on the cumulative reaction (reaction 6). Nonetheless, we recommend that reaction 3 and the corresponding equilibrium constant be used instead for cases where the redox conditions differ from those considered in this paper.

4.5.3. Transport of Au by Hydrothermal Fluids

This experimental study provides data essential for understanding the solubility and transport of gold by low-density vapours. As shown in this paper and in Archibald et al. (2001), formation of the species AuCl·(H₂O)_n or AuS·(H₂O)_m, with hydration numbers over 2 will greatly enhance the solubility and transport capacity of a vapour containing >90% H₂O at temperatures between 300 and 400 °C and pressures below 260 bar, provided that chloride and/or reduced sulphur are available for complexation of gold. Aqueous vapours containing up to 6 mol.% H₂S and HCl are found in subduction-related environments (see reviews of Williams-Jones and Heinrich, 2005; Webster and Mandeville, 2007 and references therein), i.e., in porphyry and epithermal magmatic-hydrothermal systems.

Several authors, e.g., Bernard et al. (2006) and Johnson et al. (2010), have noted that gases exsolving during the early stages of decompression-induced degassing of a magma tend to be enriched in sulphur relative to chlorine, whereas the opposite is commonly the case for those exsolved later, including post-eruptive volcanic gases. Transport of gold by vapour as hydrated sulphide species will therefore be favoured in the early stages of degassing and transport as hydrated chloride species during the waning stages of degassing, assuming appropriate physicochemical conditions. This hypothesis is supported by recent findings of Nadeau et al. (2010), showing that the amounts of sulphur and copper emitted by Merapi volcano, Indonesia, immediately after an eruption are significantly higher than during periods of quiescent degassing (orders of magnitude higher in the case of the copper). Although gold concentration was not measured by Nadeau et al. (2010), it is reasonable to assume that this metal behaves similarly (gold has an even greater affinity for sulphur than copper) and that both copper and gold were transported in the sulphur-rich vapours of Merapi volcano as species of the type discussed in this paper.

Based on analyses of volcanic gases from Merapi volcano (Nadeau et al., 2010; Nadeau et al., in preparation), we have modeled the transport of gold in a hypothetical vapour-based hydrothermal system analogous to that of high-sulphidation epithermal environments. The conditions considered are a temperature of 350 °C, pressures of 100 and 400 bar, and concentrations of S (H₂S/SO₂ ~10) and Cl in the vapour of respectively, 0.5 and 0.25 mol.% immediately after an eruption and 0.02 and 0.15 mol.% during periods of quiescence. According to our model, which is based on the results of the current study and experimental studies of Archibald et al. (2001) and Zezin et al. (2007),

the concentration of gold in the vapour ranges from 0.02 to 1 ppb during onset of a new cycle of degassing, and from 0.01 to 0.4 ppb in later stages of this cycle. Significantly, the contribution of sulphide species to the transport of gold after an eruption is approximately 50 and 40% at 100 and 400 bar, respectively, whereas during quiescent degassing of the magma, it is only about 5% (about 95% of the gold is dissolved as hydrated chloride species).

The stability of hydrated and H₂S-solvated gold sulphide complexes also depends on f_{H_2} . Specifically, the solubility of gold in the vapour increases with a decrease of f_{H_2} (in other words, as the fluid becomes more oxidized; shown by reactions 2 and 3). However, a decrease in f_{H_2} will produce a decrease in f_{H_2S} , if the composition of the vapour is buffered by the system H₂S-SO₂ (Giggenbach, 1987). There will thus be a gold solubility maximum and this will correspond to conditions for which the negative effect on f_{H_2S} of a decrease in f_{H_2} is balanced by the positive effect of this decrease on f_{O_2} . This maximum should thus occur close to the H₂S/SO₂ buffer boundary. Indeed, the calculated solubility maximum of gold as a sulphide complex at 350 °C for a total sulphur content of 0.5 mol/kg occurs at conditions that are very close to but slightly more reducing than those of equal predominance of H₂S and SO₂ (Fig. 4.5). Moreover, as might be expected, the predominance boundary and gold solubility maximum are displaced to higher f_{H_2} as pressure increases. Similar conclusions can be drawn from the results of experiments conducted at much higher temperature by Zajacz et al. (2010), who concluded that magmas at f_{O_2} conditions below the H₂S-SO₂ predominance boundary



Figure 4.5. The distribution of SO₂ and H₂S (a) and the concentration of sulphidecomplexed gold (b) in the vapour as a function of f_{H_2} calculated using the data in Zezin et al. (2007) and this study. The black lines are for a pressure of 100 bar and the grey lines for a pressure of 400 bar. The vertical dotted lines indicate conditions of maximum gold concentration and are located close to the conditions of equal predominance of SO₂ and H₂S (see text for further details).

have a better potential for releasing Au-rich volatiles than magmas at f_{O_2} conditions above it.

Using the above data it is possible to estimate the time needed to form an economically exploitable resource of gold (a hypothetical deposit) from vapour. For example, at Merapi volcano, the SO₂ emission rate is ~100 ton/day (Symonds et al., 1987), for which the concentration of sulphur in the vapour is 0.5 mol.%, corresponds to a total gas discharge of about 5000 ton/day. Assuming an average solubility of gold in the vapour of 0.5 ppb (see above), this flux of hydrothermal vapour could lead to the formation of a gold deposit containing 30 tons of Au (> 1 million oz.) in about 30 thousand years, which is well within the lifetime of many magmatic-hydrothermal systems (cf., Page and McDougall, 1972; Arribas et al., 1995; Shinohara and Hedenquist, 1997; Parry et al., 2001).

4.6. CONCLUSIONS

The principal contribution of this study has been to provide a set of data on the stability of volatile gold complexes that permits quantitative modeling of the transport of gold at temperatures up to 365 °C in natural, vapour-dominated hydrothermal systems containing reduced sulphur. From the known stoichiometry and stability of gold species in low-density fluids, i.e., the equilibrium constants of their formation reactions, it is possible to calculate the amount of gold that can be dissolved by these fluids. The results of our experiments show that the solubility of gold in H_2O-H_2S gas mixtures at temperatures of 300, 350 and 365 °C is facilitated by the formation of both solvated (by H_2S) and

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hydrated sulphide species, i.e., AuS·(H₂S)_n and AuS·(H₂O)_m. At these temperatures, the concentration of dissolved Au in the experimental fluid reached 2.2, 6.6, and 6.3 μ g/kg, respectively. Although the experiments were conducted at values of f_{H_2} buffered by the S/H₂S redox pair, the data can be used to estimate the contribution of sulphide complexes to the solubility of gold in vapours of different oxidation states using the reactions proposed for the formation of volatile gold species. An important finding of our study is that hydration of the volatile gold sulphide species has a large positive effect on their stability. Consequently, the capacity of the hydrothermal vapour to transport gold is very dependent on the partial pressure of H₂O, assuming that sufficient amounts of reduced sulphur are available for complexation with the gold. Owing to the redox dependence of the gold dissolution reaction, the maximum gold solubility in H₂S-bearing vapours is expected to be at conditions close to H₂S/SO₂ gas buffer. At these conditions, a 30 ton gold deposit could form by vapour transport of the metal within the lifetime of many magmatic-hydrothermal systems.

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Chapter 5

Conclusions and contributions to knowledge

5.1. CONCLUSIONS

- Solubility experiments conducted at temperatures between 300 and 400 °C demonstrate that appreciable quantities of gold can dissolve in H₂S gas and H₂O-H₂S gas mixtures.
- 2. In the case of a fluid consisting dominantly of H₂S gas, the species controlling the solubility of gold is a solvated sulphide complex with the stoichiometry $AuS \cdot (H_2S)_n$. This species forms as a result of the reaction:

$$Au(s) + (n+1)H_2S(g) = AuS \cdot (H_2S)_n(g) + H_2(g)$$

where n is the solvation number.

- 3. The solvation number (*n*), which represents the statistical number of molecules of H_2S in a solvation shell immediately adjacent to the molecule *AuS*, ranges from 1.8 at 300 °C to 2.2 at 400 °C. The logarithms of equilibrium constants for the reaction forming $AuS \cdot (H_2S)_n$ range from -14.9 at 300 °C to -14.2 at 400 °C, and can be used to calculate the solubility of gold in H_2S gas under conditions for which the fugacity of H_2 is also known.
- 4. Where a gas in the system H_2O-H_2S is dominated by H_2O , as is the case in most natural hydrothermal vapours, the species controlling the solubility of gold is a

hydrated gold sulphide complex with the stoichiometry $AuS \cdot (H_2O)_m$. This species forms as a result of the reaction:

$$Au(s) + H_2S(g) + mH_2O(g) = AuS \cdot (H_2O)_m(g) + H_2(g)$$

where *m* is the hydration number.

- 5. As the properties of H₂O-H₂S gas mixtures were poorly known at elevated temperature and pressure, experiments were conducted that yielded *PVTx* data at temperatures up to 400 °C. These data were fitted to a cubic equation of state that was used to calculate the properties of H₂O-H₂S gas mixtures at any conditions within the range considered by the experiments. A set of system-specific binary interaction parameters for the mixing rules of the selected equations of state were adjusted using independent experimental measurements of the properties of H₂O-H₂S system. These parameters allow quantitative estimation of the properties of the vapour and phase equilibrium calculations for H₂O-H₂S fluid mixtures at temperatures up to 400 °C.
- 6. Using the *PVTx* properties of H₂O-H₂S gas mixtures determined as a part of this study, hydration numbers and equilibrium constants were calculated for the reaction forming the species AuS · (H₂O)_m. The hydration numbers (m) range from 2.3 at 300 °C to 2.2 at 365 °C and the equilibrium constants from -15.3 at 300 °C to -15.1 at 365 °C. These data allow the solubility of gold in reduced sulphur-bearing hydrothermal fluids to be quantitatively assessed.

- 7. The solubility of gold in sulphur-bearing hydrothermal fluids reaches a maximum because of the opposing effects of the fugacity of f_{H_2S} and f_{H_2} on gold solubility (in the system H₂O-H₂S the fugacity of H₂S is lowered by the formation of SO₂ at low f_{H_2}). Model calculations show that the maximum gold solubility occurs very close to but on the H₂S side of the H₂S/SO₂ predominance boundary. These conditions are commonly encountered in natural vapour-dominated hydrothermal systems (Giggenbach, 1987) and correspond to slightly more reducing environments than those of the H₂S-SO₂ gas buffer.
- 8. It is estimated that as much as 1 μ g/kg of gold can be dissolved in H₂S-bearing aqueous vapours at optimal physicochemical conditions due to the formation of hydrated and solvated (by H₂S) gold sulphide species. This is sufficient to form an economic deposit of gold (>1 million oz.) in < 30 Ka, which is less that the lifetime of most magmatic-hydrothermal systems.

5.2. SCIENTIFIC CONTRIBUTION AND SIGNIFICANCE

This study represents an important step in understanding the behaviour of gold in H₂Sbearing vapours at elevated temperature and pressure, contributes to a database on the thermodynamic properties of volatile metallic species, and therefore, will facilitate the modeling of gold ore forming processes in vapour-dominated hydrothermal systems. The finding that gaseous sulphide species of gold can significantly enhance the dissolution and transport capacity of aqueous vapour helps in the interpretation of many natural observations, and analyses of fluid inclusions and volcanic gases, that offer empirical evidence for the transport of gold by vapour in magma-related hydrothermal systems. More particularly, the data obtained from the experiments reported in this study will improve our ability to quantitatively evaluate the vapour transport of gold in porphyry and epithermal ore-forming environments. By facilitating the modeling of processes occurring in hydrothermal systems, the study will contribute to the development of exploration tools for some types of gold deposits.

The chapter in this thesis addressing the behaviour of water-hydrogen sulphide fluid mixtures was conducted to help in calculating and modeling the properties of natural H₂S-bearing aqueous vapours. Prior to this study, there were very few data on the properties of H₂O-H₂S gas mixtures at elevated temperature and no equation of state that could adequately model these properties. The optimized parameters of the equations of state for H₂O-H₂S gas mixtures presented in this thesis will greatly extend the applicability range of these equations. The behaviour of the H₂O-H₂S fluid mixture can now be constrained in both the vapour-only and liquid-vapour stability fields at

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temperatures up to 400 °C. The detailed knowledge of the PVTx properties of H₂O-H₂S fluids resulting from this study and the ability to accurately calculate the fugacity of the components in this system will be of great help in studies of fluid inclusions, geothermal and hydrothermal fluid flow modeling, and experimental investigations of metal solubility and complexation in aqueous liquids and vapours containing hydrogen sulphide.

5.3. RECOMMENDATIONS FOR FUTURE WORK

Although the data recently obtained on the speciation and stability of sulphide and chloride complexes in the gas phase show that solvation can greatly increase the solubility of gold in the vapour (Archibald et al., 2001 and this study), they fail to explain the exceptionally high concentrations of gold that have been reported from analyses of vapour-rich fluid inclusions (e.g., Ulrich et al., 1999; Seo et al., 2009). The discrepancy between the solubility of gold calculated from the experimental data and observed in natural fluid samples reaches two to three orders of magnitude. Even greater concentrations of gold (tens to hundreds $\mu g/g$) have been reported in vapours trapped as fluid inclusions from experiments conducted at magmatic temperatures (800-1000 °C; see Simon et al., 2007; Zajacz et al., 2010). The experiments of the type reported here will need to be extended to much higher temperature and pressure (400-700 °C and 300-1000 bar) to help resolve this discrepancy and may need to consider ligands other than sulphide and chloride (e.g., other more oxidized sulphur species such as sulphates or sulphites). They may also need to involve other solvents (e.g., SO₂, CO₂). Most previous

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solubility studies, including those presented in this thesis, were conducted in titanium or titanium alloy cells, materials that impose severe limitations on the temperature of experiments; above 450 °C these materials are very brittle and the autoclaves invariably fail. If other chemically and thermally resistant materials and alloys could be identified, autoclaves could be built (the laboratory is currently testing autoclaves constructed from zirconium) and that would allow the solubility of gold and other important elements to be measured at magmatic temperatures, and thus be relevant for studies of the behaviour of gold in porphyry ore-forming environments.

This study was initially designed to investigate the solubility of copper in reduced sulphur-bearing vapours. Unfortunately, because of problems with contamination and insufficient solubility in the vapour due to precipitation of copper sulphide minerals, the study was abandoned in favour of a study focussed on gold. However, copper, like gold, has a great affinity for reduced sulphur and can be expected to form volatile sulphide complexes. Furthermore, there is evidence from analyses of fluid inclusions that natural vapours can dissolve exceptionally high concentrations of copper (in excess of 3 wt.%), and that copper, like gold, partitions preferentially into the vapour phase relative to a liquid in magmatic-hydrothermal systems (e.g., Lowenstern et al., 1991; Heinrich et al., 1992; Ulrich et al., 1999). There is thus great incentive to comprehensively evaluate the behaviour of copper in aqueous vapours experimentally. As is the case for gold, the solubility of copper has been determined in H₂O-HCl vapours (Archibald et al., 2002) and there have been investigations of its speciation using spectroscopic methods (Pokrovski et al., 2008; Etschmann et al., 2010). However, there have been no studies of the solubility of copper in sulphur-bearing vapours or vapours containing other

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potentially important ligands. Such studies need to be carried out in order to understand the apparent ability of natural vapours to transport high concentrations of copper and improve upon existing models for the formation of Cu porphyry deposits, the principal sources of this metal, globally.

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