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# Gold speciation and transport in geological fluids: insights from experiments and physical-chemical modelling

GLEB S. POKROVSKI<sup>1\*</sup>, NIKOLAY N. AKINFIEV<sup>2</sup>, ANASTASSIA Y. BORISOVA<sup>1,3</sup>, ALEXANDRE V. ZOTOV<sup>2</sup> & KALIN KOUZMANOV<sup>4</sup>

<sup>1</sup>Géosciences Environnement Toulouse, GET (ex-LMTG), Université de Toulouse, CNRS-IRD-OMP, 14 Av. E. Belin, F-31400 Toulouse, France

<sup>2</sup>Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry Russian Academy of Sciences, Staromonetny per. 35, 119017 Moscow, Russia

<sup>3</sup>Geological Department, Moscow State University, Vorobevu Gory, 119899 Moscow, Russia

<sup>4</sup>Earth and Environmental Sciences, University of Geneva, rue des Maraîchers 13, CH-1205 Geneva, Switzerland

\*Corresponding author (e-mail: gleb.pokrovski@get.obs-mip.fr)

Abstract: This contribution provides an overview of available experimental, thermodynamic, and molecular data on Au aqueous speciation, solubility, and partitioning in major types of geological fluids in the Earth's crust, from low-temperature aqueous solution to supercritical hydrothermalmagmatic fluids, vapours, and silicate melts. Critical revisions of these data allow generation of a set of thermodynamic properties of the AuOH, AuCl<sub>2</sub>, AuHS, and Au(HS)<sub>2</sub> complexes dominant in aqueous hydrothermal solutions; however, other complexes involving different sulphur forms, chloride, and alkali metals may operate in high-temperature sulphur-rich fluids, vapours, and melts. The large affinity of Au for reduced sulphur is responsible for Au enrichment in S-rich vapours and sulphide melts, which are important gold sources for hydrothermal deposits. Thermodynamic, speciation, and partitioning data, and their comparison with Au and S contents in natural fluid inclusions from magmatic-hydrothermal gold deposits, provide new constraints on the major physical-chemical parameters (temperature, pressure, salinity, acidity, redox) and ubiquitous fluid components (sulphur, carbon dioxide, arsenic) affecting Au concentration, transport, precipitation, and fractionation from other metals in the crust. The availability and speciation of sulphur and their changes with the fluid and melt evolution are the key factors controlling gold behaviour in most geological situations.

Since alchemists' times, the reputation of gold has been to be the most noble of the metals, that is, existing as a native metal in the solid phase at all terrestrial conditions and being extremely unreactive in contact with most liquids and gases. However, the existence of magmatic-hydrothermal gold ores unambiguously attests that gold may be concentrated, transported, and deposited by geological fluids in quantities sufficient to form an economic deposit, in which this metal is enriched by factors of 1000-10 000 compared to its average concentration in the Earth's crust (c. 1 ppb, Rudnick & Gao 2003). Detailed knowledge of aqueous chemistry and solubility of Au in geological fluids over a wide range of temperatures and pressures is thus necessary for understanding Au distribution and concentration in the crust.

The solubility of gold has been the subject of numerous alchemical, industrial, experimental, theoretical, and geologic studies for hundreds of years (e.g. see Williams-Jones *et al.* 2009 for a

historical overview). Despite the large amount of information on Au geo(chemistry) gained so far, many questions remain about the physical-chemical and geological processes and mechanisms that control Au mobilization and deposition, particularly under hydrothermal conditions at which most Au ores form. An approach combining experimental data, physical-chemical modelling, and geological observations is necessary to quantify the impact of these processes on the gold fate and distribution. Probably the first quantitative account of Au solubility in hydrothermal solutions was done by Krauskopf (1951) who attempted to interpret the few Au solubility experiments available at that time (Ogryzlo 1935; Smith 1943; references therein) in terms of Au speciation and thermodynamics in solution. These works provided the foundation for our understanding of Au hydrothermal chemistry that is controlled by chemical entities or species with sulphur, chloride, and oxygen, although the proposed stoichiometry of these

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species was tentative at that time. About twenty years later, Helgeson & Garrels (1968) applied in their paper an integrated approach combining rare available experimental data, thermodynamic extrapolations of Au solubility, and considerations of the budget of Au and accompanying elements in gold veins based on geological observations. Their conclusions about Au transport in hydrothermal fluids as aurous chloride species precipitating in response to cooling were, however, criticized by Boyle (1969) who, based on field observations and geochemistry of Au ores, argued that Au is primarily transported as complexes with S, As, and Sb and is deposited in response to decompression and fluid-rock interaction rather than cooling.

The following 45 years of efforts of many other ore deposit geologists, experimentalists, and thermodynamists studying Au in all its facets in hydrothermal fluids, silicate melts, and minerals, have not significantly changed the state of this debate. Today, even if we know far better a substantial part of possible Au chemical species carrying this metal in geological fluids, we have still rather limited data on Au contents and distribution in hydrothermal fluids from direct analyses of fluid inclusions and in volcanic gases and geothermal systems, and we always wonder why Au in its ores is associated with some particular elements in particular phases (e.g. arsenian pyrite) or CO<sub>2</sub>-bearing fluids. With the rapidly growing progress in experimental, spectroscopic, analytical, and modelling techniques, our knowledge of Au chemistry in hydrothermal fluids, magmatic vapours, silicate melts, and solid phases is expanding rapidly, particularly in the last 10-15 years. However, the application of these results to gold ore deposits is always faced with the fascinating complexity of natural processes responsible for Au mobilization, concentration, and deposition.

The present contribution is a humble attempt to summarize what we have learned about gold in geological fluids over the more than 50 years since the pioneering experimental and theoretical works cited above, and how this knowledge may help to better constrain our understanding of the impact of different factors leading to the formation of gold ore deposits. In this paper, we first give an overview of the available experimental and thermodynamic data on Au aqueous speciation and solubility over a wide range of geological fluid conditions, from low-temperature aqueous solution to supercritical hydrothermal fluids, volcanic gases, and silicate melts. Next, on the basis of these data, we quantify the effect on Au solubility of major parameters and components typical of geological fluids (temperature, pressure, salinity, acidity, redox, sulphur, CO<sub>2</sub>, arsenic). Then, we compare thermodynamic predictions with natural Au contents from direct analyses of fluid inclusions from porphyry

Cu-Au-Mo and associated deposits. The confrontation between natural data and physical chemistry provides useful contraints on understanding the mechanisms and processes (cooling, decompression, boiling, water-rock interactions, fluid mixing) controlling Au transport and deposition in different types of deposits, which are discussed in a separate section. Finally, we identify several remaining gaps in our knowledge of Au hydrothermal chemistry and discuss experimental, analytical, and modelling challenges expected to help reduce these gaps in the near future.

# Overview of experimental and theoretical data on Au speciation and solubility in magmatic-hydrothermal fluids

#### General features of gold aqueous chemistry

Detailed knowledge of aqueous chemistry of Au over a wide range of temperature and pressure is crucial for understanding Au distribution and concentration by crustal fluids in various geological environments. This section briefly outlines the major features of Au aqueous speciation and molecular coordination.

Gold possesses the complete electronic structure [Xe]  $5d^{10}6s^1$  and, like silver and copper, has a single *s*-electron outside a completed *d*-shell. Despite large similarities of outer-shell electronic configurations and ionization potentials, there are significant differences amongst these metals as to their redox forms and affinities to different ligands. There is no simple explanation of these differences, but some of them are likely to be due to relativistic effects on the 6*s*-electrons of Au (Cotton & Wilkinson 1988).

Although Au shows a wide range of oxidation states, from I to VII, in synthetic chemical compounds, apart from Au<sup>0</sup>, the dominant oxidation states of chemically-bound Au in natural fluids and minerals are trivalent (auric gold, Au<sup>III</sup>) and monovalent (aurous gold, Au<sup>1</sup>). The former is, however, a strong oxidant and is stable only in oxidizing surface environments, whereas the latter is the dominant Au form in the majority of hydrothermal fluids and silicate melts (e.g. Pokrovski et al. 2009a, b; references therein). Both in solid phase and aqueous solution, Au<sup>III</sup> is almost always coordinated with four ligands in a square geometry (Puddephatt 1978; Schwerdtfeger et al. 1992; Farges et al. 1993; see Table 1), whereas Au<sup>1</sup> systematically forms linear two-coordinate structures at naturally pertinent conditions (Schwerdtfeger et al. 1992; Tossell 1996), with only the few exceptions of 3- and 4-coordinate Au<sup>I</sup> in some synthetic metallo-organic compounds (e.g. Benfield et al.

Complex	Au-ligand bond	Au coordination geometry	Mean distance, Å	Conditions	References
AuCl <sub>2</sub>	Au <sup>I</sup> -Cl	Linear	$2.267\pm0.004$	Au-NaCl-HCl-AuCl <sub>4</sub> aqueous solution, 250 °C, 600 bar	Pokrovski et al. (2009a)
AuCl <sub>4</sub>	Au <sup>III</sup> –Cl	Square-planar	$2.28\pm0.01$	HAuCl <sub>4</sub> -HCl-NaCl aqueous solution, ambient <i>T</i>	Benfield <i>et al.</i> (1994); Berrodier <i>et al.</i> (2004); Pokrovski <i>et al.</i> (2009 <i>a</i> )
$Au(OH)_nCl_{4-n}$	Au <sup>III</sup> –O Au <sup>III</sup> –Cl	Square-planar	$\begin{array}{c} 1.99 \pm 0.02 \\ 2.28 \pm 0.01 \end{array}$	HAuCl <sub>4</sub> -NaOH-NaCl aqueous solution, ambient <i>T</i>	Farges <i>et al.</i> (1993); Berrodier <i>et al.</i> (2004); Song <i>et al.</i> (2012)
$*Au(CN)_2^-$	Au <sup>I</sup> –C	Linear	1.98 - 2.12	$Au(CN)_2^-$ -bearing salts	Wang et al. (2009); refs therein
$Au(S_2O_3)_2^{3-}$	Au <sup>I</sup> -S	Linear	$2.30\pm0.01$	Na <sub>3</sub> Au(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> aqueous solution, ambient $T-P$	Bryce <i>et al.</i> (2003); Pokrovski <i>et al.</i> (2009b)
$Au(HS)_2^-$	Au <sup>I</sup> -S	Linear	2.29 ± 0.01	Au-S-NaOH aqueous solution, pH > 5, 200-450 °C, 1–1000 bar	Pokrovski et al. (2009b)
<sup>†</sup> AuHS(H <sub>2</sub> S), Au–S <sub>n</sub> , AuHS(SO <sub>2</sub> )	Au <sup>I</sup> –S	Linear	2.29 ± 0.01	Au-S-Na <sub>2</sub> SO <sub>4</sub> aqueous solution, pH < 4-5, 300-450 °C, 1-1000 bar	Pokrovski et al. (2009b)

Table 1. Gold coordination and Au-ligand interatomic distances in geologically relevant aqueous Au complexes measured by in situ X-ray absorption spectroscopy

\*X-ray and neutron diffraction; no XAS data are available for aqueous species. <sup>†</sup>Tentative stoichiometries (see section "The role of other sulphur-bearing forms for hydrothermal transport of gold" and Pokrovski *et al.* 2009*b* for detailed discussion).

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1994; ICSD 2010; references therein). This rather simple Au coordination contrasts with the large variety of Cu<sup>I</sup>, Cu<sup>II</sup>, and Ag<sup>I</sup> first-shell geometries both in solids and solution, from 2- to 6-coordinate such as linear, trigonal, distorted tetragonal, pyramidal or octahedral (e.g. Cotton & Wilkinson 1988; ICSD 2010; Pokrovsky et al. 2012; Pokrovski et al. 2013a). Gold-ligand interatomic distances in the main geologically relevant species in aqueous solution have been recently determined using direct measurements by X-ray absorption spectroscopy (XAS, Table 1). These distances are pretty constant for each ligand type (OH/H<sub>2</sub>O, Cl or S) and almost independent of temperature and pressure, thus confirming the strong covalent nature of Au-ligand bonds and the constancy of Au coordination over a wide T-P range. The stability of main Au<sup>III</sup> and Au<sup>I</sup> species with naturallyrelevant ligands is discussed below.

Among natural ligands capable of complexing  $Au^{III}$  in aqueous solution, the  $Cl^-$  and  $OH^-$  ions are the most common. Studies at room temperature indicate that  $Au^{III}$  is strongly hydrolysed over a wide pH range, but the identity and stability of hydroxide species are poorly constrained because of low solubilities and formation of unstable solid phases (e.g.  $Au(OH)_3$ ) and Au colloids (Baes & Mesmer 1976; references therein). As a result, the thermodynamic properties of the  $Au^{3+}$  cation, which is expected to form only in extremely acidic noncomplexing media, are poorly known, and only

few theoretical estimates exist in the literature (Table 2).

The famous  $AuCl_4^-$  complex is responsible for gold dissolution in aqua regia (i.e. a mixture of concentrated HCl and HNO<sub>3</sub>). Its structure and stability have been studied in detail at oxidizing near-ambient conditions using potentiometry (Nikolaeva et al. 1972), Raman (Pan & Wood 1991; Peck et al. 1991; Murphy & Lagrange 1998), UV-visible (Usher et al. 2009), NMR (Sharps et al. 1993), and X-ray absorption spectroscopy (Farges et al. 1993; Berrodier et al. 2004; Pokrovski et al. 2009a; see Table 1). This complex is dominant in acidic solutions  $(pH \le \sim 5)^{-}$  and, with an increase in solution pH, is progressively replaced by mixed AuCl<sub>n</sub>(OH)<sup>-</sup><sub>4-n</sub> species (where  $0 \le n \le 4$ ), with total gold solubility dropping in neutral-to-basic solutions. On heating of acidic Au<sup>III</sup> chloride solutions, gold is rapidly reduced to Au<sup>I</sup> even under highly oxidizing conditions (Pokrovski et al. 2009a). In natural aquatic systems, the presence of reducing agents (e.g. sulphide, organic matter, ferrous iron) will further tend to reduce Au<sup>III</sup> to Au<sup>I</sup> or Au<sup>0</sup>. Thus, the natural settings where Au<sup>III</sup> species may be important are limited to welloxygenated, highly saline acidic groundwaters (Usher et al. 2009) and/or Fe<sup>III</sup> and Mn<sup>IV</sup> oxyhydroxide mineral surfaces (Berrodier et al. 2004).

The aurous cation,  $Au^+$ , is one of the softest cations in solution, according to the soft-hard classification of Pearson (1963) that suggests that large,

Reaction	log K 25 °C, 1 bar	References
$Au^{3+} + 4Cl^{-} = AuCl_{4}^{-}$ $Au^{+} + 2CN^{-} = Au(CN)_{2}^{-}$ $Au^{+} + 2SCN^{-} = Au(SCN)_{2}^{-}$	26.2 38.7 17.0	Nikolaeva <i>et al.</i> (1972)* Seward (1989) <sup>†</sup> Martell <i>et al.</i> (2004) <sup>‡</sup>
$Au^{+} + OH^{-} = AuOH^{0}$ $Au^{+} + CI^{-} = AuCl^{0}$ $Au^{+} + 2Cl^{-} = AuCl_{2}^{0}$	10.2 7.9 9.6	Kissner <i>et al.</i> (1997) Akinfiev & Zotov (2010) Akinfiev & Zotov (2010)
$Au^{+} + 2Br^{-} = AuBr_{2}^{-}$ $Au^{+} + 2I^{-} = AuI_{2}^{-}$ $Au^{+} + HS^{-} = Au(HS)^{0}$ $Au^{+} + 2HS^{-} = Au(HS)^{-}$	12.4 19.0 24.6 30.2	Seward $(1989)^{\dagger}$ Seward $(1989)^{\dagger}$ Akinfiev & Zotov (2010) Akinfiev & Zotov (2010)
$Au^{+} + 2S_{2}O_{3}^{2^{-}} = Au(S_{2}O_{3})_{2}^{3^{-}}$ $Au^{+} + 2S_{2}O_{3}^{2^{-}} = Au(S_{2}O_{3})_{2}^{3^{-}}$	26.0 26.8	Seward $(1989)^{\dagger}$ Webster $(1986)^{\dagger}$
$Au(s) + H^+ = Au^+ + 0.5 H_2(g)$ $Au(s) + 3H^+ = Au^{3+} + 1.5 H_2(g)$	-28.6 -75.9	Shock <i>et al.</i> (1997) Shock <i>et al.</i> (1997)

**Table 2.** Stability constants of main aqueous  $Au^{III}$  and  $Au^{I}$  complexes at 25 °C and Ibar according to available literature data

\*Recalculated to zero ionic strength using the  $AuCl_{2}^{-}/AuCl_{4}^{-}$  standard potential (Nikolaeva *et al.* 1972), and Gibbs free energies of  $Au^{3+}$  and  $AuCl_{2}^{-}$  from Shock *et al.* (1997) and Akinfiev & Zotov (2001), respectively. <sup>†</sup>Compiled/recalculated from older studies.

<sup> $\ddagger$ </sup>Ionic strength = 3.0.

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weakly charged, and easily polarizable cations, termed 'soft' (e.g. Au, Ag, Hg, Pt) form the strongest covalent complexes with 'soft' anions having similar properties (e.g. HS<sup>-</sup>, CN<sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, Br<sup>-</sup>,  $I^{-}$ ), whereas small, highly charged, and/or not easily polarizable cations termed 'hard' (e.g. alkaline earth metals, rare earth elements, Al, Zr) preferentially form stable ionic-bond complexes with 'hard' anions of similar properties (e.g.  $F^-$ ,  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $OH^{-}$ ). Intermediate between these two extremes are metals (e.g. Cu, Fe, Zn) and ligands (e.g.  $Cl^-$ ,  $SO_3^{2-}$ ,  $NH_3$ ) called 'borderline'; they tend to form between them the most stable complexes. Because of the higher charge and weaker polarizability, Au<sup>III</sup> is harder than Au<sup>I</sup>, which explains its preference to Cl<sup>-</sup> (see above). It follows from the soft-hard affinity rules that Au<sup>1</sup> is unlikely to form stable complexes with hard ligands like fluoride, carbonate, or sulphate. Indeed, no stability constants are known for such species. The stability constants of Au<sup>III</sup> and Au<sup>I</sup> complexes with typical naturally-relevant ligands are summarized in Table 2. The strongest Au<sup>I</sup> inorganic complex, known so far in aqueous solution, is dicyanide,  $Au(CN)_2^-$ , which is widely used for leaching of Au from its ores (e.g. Muir 2011 for a recent review). This and other soft ligands, such as  $S_2O_3^{2-}$ , SCN<sup>-</sup>, and thiol (-S<sup>II</sup>) and amid (-N<sup>III</sup>) functional groups of fulvic and humic acids, produced by decomposition of plants and algae via microorganism activity, or by pyrite and sulphur oxidation, may contribute to the transport of Au<sup>1</sup> in surface waters and mine drainage sites (e.g. Vlassopoulos et al. 1990). Some of these ligands, being less toxic than CN<sup>-</sup>, are considered as alternatives to cyanide for selective extraction of Au from hydrothermal ores (e.g. Adams 2005).

It should be noted that the chemical affinity of a metal and a ligand themselves (which may be quantified by the thermodynamic constant of a complex formation reaction, Table 2) is not the only property governing metal speciation in natural fluids. The availability (i.e. concentration or activity) of the ligand is another major controlling factor. Thus, in a dilute aqueous solution, devoid of the soft ligands discussed above. Au<sup>1</sup> prefers the hydroxide over the water ligand and is thus hydrolysed by forming the neutral AuOH complex over a wide pH range (e.g. Vlassopoulos & Wood 1990). Although hydroxide is rather hard, it is strongly basic and thus a good donor for Au<sup>1</sup>, which may be explained by relativistic contraction of the 6 s orbital of  $Au^{I}$  (Kissner *et al.* 1997). Thus, similarly to  $Au^{3+}$  (see above), the free  $Au^{+}$ cation is unstable in aqueous solution; as a result, its thermodynamic properties are poorly known (Table 2). Despite the stability constant values of Au<sup>I</sup>-CN and Au<sup>I</sup>-I complexes are 9-10 orders of magnitude higher than those of their Au<sup>I</sup>–SH and Au<sup>I</sup>–I v. Au<sup>I</sup>–Cl analogues (Table 2), the extremely low concentrations of cyanide and iodide in most natural waters, particularly under hydrothermal conditions, render their complexes almost negligible. Thus, the major carriers of gold in geological fluids at elevated temperatures are hydroxide, chloride, and hydrogen sulphide (and possibly some other sulphur forms such as polysulphides in S-rich fluids) as will be shown below.

## Gold chloride, hydrogen sulphide, and hydroxide species in aqueous solution and dense supercritical fluid

Despite the almost 50-year work on gold in the earth science community, experimental data on gold solubility and aqueous speciation in the presence of major natural ligands-chloride, hydroxide, and hydrogen sulphide-are not sufficiently systematic and consistent. Thermodynamic reviews of Sverjensky et al. (1997) allowed generation of a first set of thermodynamic properties of  $Au(HS)_2^{-1}$ and Au<sup>I</sup> and Au<sup>III</sup> chloride species based on rare existing experiments. However, these data were subject to large uncertainties because the parameters of these Au species were based on empirical correlations for the Au<sup>+</sup> ion whose properties are not accurate enough (see the section above). Another thermodynamic review published four years later (Akinfiev & Zotov 2001) allowed generalizing the strategy of analysis of experimental information available at that time on the stability constants of Au<sup>1</sup> chloride, hydrogen sulphide, and hydroxide complexes. Recently published experimental data on the stability of Au hydrogen sulphide complexes both at low (Tagirov et al. 2006) and high temperatures (Stefánsson & Seward 2004; Tagirov et al. 2005) have been considered in a more recent summary (Akinfiev & Zotov 2010). In this section, after a systematic compilation of the available experimental data of Au speciation in hydrothermal chloride- and sulphide-bearing solutions, we present a thermodynamic database for aqueous species in the Au-S<sup>-II</sup>-Cl-O-H system applicable over a wide range of temperatures (0-600) $^{\circ}$ C) and pressures (1–3000 bars).

*Historical background.* To the best of our knowledge, the first laboratory investigations of gold solubility in model aqueous solutions at hydrothermal conditions in the presence of chloride and sulphide have been those of Ogryzlo (1935) and Weissberg (1970). Although these works were lacking the modern-day accuracy of chemical analyses of aqueous solutions, they have allowed establishing the principal forms of Au in solution (hydroxide,

chloride, and sulphide complexes) and thus determined the subsequent research directions in the experimental geochemistry of Au in hydrothermal fluids. The following step in this research was marked by studies of Seward (1973) on Au hydrogen sulphide species and Henley (1973) on chloride complexes under controlled oxygen (or hydrogen) fugacity, and by the potentiometric work of Nikolaeva et al. (1972) who reported the stabilities of Au<sup>I</sup> and Au<sup>III</sup> chloride species. These pioneering works were followed by a plethora of experimental reports on Au solubility and speciation in hydrothermal solutions, which are summarized in Table 3 and briefly reviewed below for the three main types of Au aqueous species formed with hydroxide, chloride, and hydrogen sulphide.

Au<sup>1</sup> hydroxide complexes. The stability of the monohydroxide species AuOH<sup>0</sup> has been investigated in detail over 20 years by the solubility method using both batch and flow-through hydrothermal reactors (Baranova *et al.* 1983; Zotov *et al.* 1985; Stefánsson & Seward 2003*a*). The results are in good agreement with one another, particularly at elevated temperatures (450–500 °C). Another solubility study (Baranova *et al.* 1977) reported the formation of the dihydroxide species, Au(OH)<sub>2</sub><sup>-</sup>, at very alkaline conditions (pH > 10), which are unlikely to occur in geological environments.

Au<sup>I</sup> chloride complexes. The thermodynamic properties of AuCl<sub>2</sub><sup>-</sup> in a wide temperature and pressure range were investigated by Zotov et al. (1989, 1991) and Stefánsson & Seward (2003b), using quench-based batch-autoclaves and samplingbased flow-through reactors, respectively. The agreement is good at 500 °C, the temperature at which chloride complexes began to be important in natural systems (see below), but at and below 400 °C the data of Stefánsson & Seward (2003b) yield AuCl<sub>2</sub><sup>-</sup> concentrations up to one order of magnitude lower than those of Zotov et al. (1989, 1991). Gammons & William-Jones (1995) employed a different method using Au-Ag alloys as redox indicators and determined the stability constant of  $AuCl_2^-$  at 300°C. Their value is in good agreement with the Stefánsson & Seward (2003b) study, and interpolations between the previous studies at low (Nikolaeva et al. 1972) and high (Zotov et al. 1989, 1991) temperatures. In contrast, there are large differences between those studies and the results of Henley (1973) and Wood et al. (1987). The former showed unusually high solubilities and large data scatter (over two orders of magnitude in Au concentration); the latter used a complex multiphase sulphide system at moderate temperatures (200-300 °C) at which it is difficult to demonstate equilibrium. Consequently, we do not recommend these two studies for the thermodynamic analysis of AuCl<sub>2</sub><sup>-</sup>. More recently, Pokrovski *et al.* (2009*a*) used *in situ* X-ray absorption spectroscopy to establish the structure of AuCl<sub>2</sub><sup>-</sup> (Table 1) and demonstrate that this species is the dominant Au chloride complex in a wide *T* and salt concentration range, and that higher-order chloride species are negligible at these conditions.

Au<sup>1</sup> hydrogen sulphide complexes. These Au species account for the major part of experimental studies of Au at hydrothermal conditions. The basic information about the stoichiometry and stability of these complexes has been obtained by Seward (1973), Renders & Seward (1989), and Shenberger & Barnes (1989). These works found that the dominant Au species in H2S-bearing solutions are AuHS<sup>0</sup> at acidic pH, Au(HS)<sub>2</sub><sup>-</sup> at near-neutral pH, and  $Au_2S_2^{2-}$  or  $Au_2(HS)_2S^{2-}$  at alkaline pH. In the numerous later studies using different types of solubility methods (Hayashi & Ohmoto 1991; Zotov & Baranova 1995; Benning & Seward 1996; Gibert et al. 1998; Stefánsson & Seward 2004; Tagirov et al. 2005, 2006), and, more recently, in situ spectroscopic methods (Pokrovski et al. 2009b), the stability of Au(HS)<sub>2</sub> at near-neutral pH, pertinent to natural fluids, has been extended across a wide T-P and compositional range. The numerical results of Au solubility from these studies have been compared by Pokrovski et al. (2009b) and reviewed by Akinfiev & Zotov (2010).

In contrast to all these studies whose results are in decent agreement, a few other solubility works diverge significantly from the main trend. For example, Baranova & Zotov (1998) reported unrealistically high  $Au(HS)_2^-$  concentrations in equilibrium with the metal; in contrast, Pan & Wood (1994) found suspiciously low solubilities. Loucks & Mavrogenes (1999) investigated Au solubility at higher T-P than all existing studies (500–700 °C, and 1-4 kbar) and found Au concentrations up to 1000 ppm, which were interpreted as a new species,  $AuHS(H_2S)_3^0$ . These data are, however, inconsistent with more recent work (see section "The role of other sulphur-bearing forms for hydrothermal transport of gold" below). The results of Fleet & Knipe (2000), who measured Au solubility in fluids with extremely high H<sub>2</sub>S contents (up to H<sub>2</sub>S mole fractions of  $\sim 0.3$ , equivalent to  $\sim 20 \text{ mol/kg}$  $H_2O$ ) and interpreted it in terms of Au(HS)<sub>2</sub>, cannot be used for rigourous derivation of thermodynamic properties of aqueous Au complexes. Consequently, the four studies cited above were not included in the following thermodynamic analysis. Gold species with sulphur ligands other than  $H_2S/HS^-$  will be discussed in section, "The role of other sulphur-bearing forms for hydrothermal transport of gold."

Year	Authors	T, °C	P, bar	System composition	Main results
1935	Ogryzlo	200-300	svp	Solubility of Au in HCl, NaCl, Na <sub>2</sub> CO <sub>3</sub> , and Na <sub>2</sub> S solutions	Observation of elevated Au solubility in alkaline sulphide solutions
1970	Weissberg	150-290	1000	Solubility of Au in alkaline solutions (0.25-0.9 m Na <sub>2</sub> S)	Elevated solubility growing with T and mNa <sub>2</sub> S
1972	Nikolaeva et al.	25-80	1	Potentiometry in KCl solutions $(I = 1)$	$E^{\circ}$ of the reaction AuCl <sub>2</sub> <sup>-</sup> + e <sup>-</sup> = Au <sub>c</sub> + 2Cl <sup>-</sup> at I = 1
1972	Gadet & Pouradier	25	1	Potentiometry in Au-Cl-Br-NaOH solutions using gold and calomel electrodes as a function of pH	Equilibrium constants between AuX <sub>2</sub> , AuXOH <sup>-</sup> , and Au(OH) <sub>2</sub> , where X = Cl or Br
1973	Seward	175–250	1000	Solubility of Au in NaHS + NaCl solutions ( $I = 0.5$ ) with PyPo buffer and pH <sub>20°</sub> ~4–10	First solubility study under fixed $f(O_2) \cdot AuHS^0$ , $Au(HS)_2^-$ , and $Au_2(HS)_2S^{2-}$ were suggested, and stability constants of the two latter species determined between 175 and 250°C
1973	Henley	300-500	1000-2000	Solubility of Au in 0.5–2.0 m KCl solutions at MH and OMF buffers	Elevated Au solubility in chloride solutions and its growth with increasing temperature
1977	Baranova <i>et al</i> .	25-200	svp	Solubility of Au in H <sub>2</sub> O and NaOH with MtHe buffer	AuOH <sup>0</sup> dominates below $pH_{25^{\circ}} \sim 12$ ; Au(OH) <sub>2</sub> appears at more alkaline pH
1981	Belevantsev et al.	20	1	Solubility of $Au_2S(s)$ in sulphide solutions at pH 6–12	Stability constants of Au(HS) <sub>2</sub> <sup>-</sup> , Au(HS)(OH) <sup>-</sup> , Au(HS)(H <sub>2</sub> S) <sup>0</sup> , and Au <sub>2</sub> (HS) <sub>2</sub> S <sup>2-</sup>
1982	Nekrasov et al.	300	1000	Solubility of Au in $Sb_2S_3-H_2S(0.065 \text{ m})-HCl$ (0.1 m) solutions	Au solubility increases with increasing Sb concentration; polynuclear Au-Sb species are suggested
1983	Baranova <i>et al</i> .	450	500	Solubility of Au in H <sub>2</sub> O at fixed log $f(O_2) = -17.3 - 27.8$	AuOH <sup>0</sup> is suggested
1984	Ryabchikov & Orlova	750	1500	Solubility of Au in acid chloride solutions in the presence of granite melt and NNO buffer	Au solubility is up to 100s ppm; it increases with increasing Cl concentration
1985	Zotov et al.	300-500	500-1500	Au solubility in pure $H_2O$ , with Ni–NiO, $Fe_2O_4 - Fe_2O_2$ , and $Cu - Cu_2O$ buffers	Formation constants of the reaction $Au + 0.5H_2O + 0.25O_2 = AuOH^0$
1987	Wood <i>et al</i> .	200-350	svp	Solubility of sulphide minerals (Fe, Sb, Zn, Pb, Ag, Bi, Mo) and Au in NaCl (0–5 m) solutions at PyPoMt buffer	$AuCl_2^-$ and $HAu(HS)_2^0$ are suggested
1989	Renders & Seward	25	1	Solubility of $Au_2S(s)$ in $H_2S$ -HS-solutions at pH 2-12 and total S 0.006-0.4 m	Stability constants of $AuHS^0$ , $Au(HS)_2^-$ , and $Au_2S_2^{2-}$

Table 3. Summary of published experimental studies on Au solubility and speciation in aqueous solution at hydrothermal conditions

(Continued)

Table 3. Continued

Year	Authors	T, °C	P, bar	System composition	Main results
1989	Shenberger & Barnes	150-350	svp	Solubility of Au in sulphide ( $S_{tot} = 0.5-1.3$ m) solutions at pH = 3-8 and fixed oxidation state by H <sub>2</sub> or H <sub>2</sub> S-SO <sub>4</sub> equilibrium	Stability constants of $Au(HS)_2^-$
1989	Zotov et al.	450	400-1000	Solubility of Au in HCl $(0-0.64 \text{ m})$ – KCl $(0-3.31 \text{ m})$ solutions at log $f(O_2) - 29$ to $-26$	The dominant species in acidic $H_2S$ -poor solutions is $AuCl_2^-$
1991	Zotov et al.	350 450 500	1000 500–1500 1000	Solubility of Au in H <sub>2</sub> O-HCl $(0.1-0.2 \text{ m})$ – KCl or NaCl $(0-0.3 \text{ m} \text{ or } 0.1-2 \text{ m})$ solutions at fixed $f(H_2)$ by addition of Al	$logK^{\circ}$ of the reaction Au + HCl <sub>aq</sub> + Cl <sup>-</sup> + 0.25O <sub>2 (g)</sub> = AuCl <sub>2</sub> <sup>-</sup> + 0.5H <sub>2</sub> O and HKF parameters for AuCl <sub>2</sub> <sup>-</sup>
1991	Hayashi & Ohmoto	250-350	svp	Solubility of Au in H <sub>2</sub> O + S <sub>c</sub> $\pm$ NaCl (0-4 m) $\pm$ Na <sub>2</sub> SO <sub>4</sub> (0-0.3 m) solutions at pH <sub>25°</sub> 1.1-1.7, and calculated log a(H <sub>2</sub> S <sub>ao</sub> ) - 2.0 to -0.7	$log K^{\circ} \text{ of reaction Au} + 2H_2 S_{(aq)} = HAu(HS)^0 + 0.5H_2$
1991	Pan & Wood	25-300	svp	Raman spectra of gold-chloride complexes in very acidic solutions (2–5 m HCl, 0.02–0.04 m Au)	Linear Au(I)-chloride complexes AuCl <sub>2</sub> <sup>-</sup> , with a single Raman band at $\sim$ 332 cm <sup>-1</sup> at $T > 100$ °C
1992	Likhoidov & Nekrasov	500-600	1000	Solubility of Au in H <sub>2</sub> O–HCl–H <sub>2</sub> SO <sub>4</sub> solutions in equilibrium with PMH, PPM, and PM buffers	Results are interpreted by the formation of different hydrogen sulphide complexes
1993	Pal'yanova <i>et al</i> .	200	500	Solubility of Au in alkaline (pH <sub>20°</sub> = 7.3–8.5) solutions at high sulphur content near sulphide-sulphate equilibrium (HS <sup>-</sup> , S <sub>2</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> )	Extremely high Au solubility (up to 1600 ppm). In addition to hydrogen sulphide complexes, thiosulphate, and polysulphide species are suggested
1994	Berndt <i>et al.</i>	100-150	100	Solubility of Au in sulphur-saturated solutions with small amounts of NaHS and NaOH/HCl, $pH = 5.5-8$ , $S_{tot} = 0.015-0.06$ m	Polysulphide species (AuS <sub>n</sub> S <sup>-</sup> , where $n = 2 - 7$ ) are suggested to be the main Au forms in solutions saturated with native sulphur
1994	Likhoidov & Nekrasov	300-500	1000	Solubility of Au in $H_2O-NaCl (1-5 m)$ solutions with PMH buffer	Results are interpreted by the formation of sulphide and chloride complexes
1994	Wood et al.	25-90	1	Solubility of Au in $H_2S$ -saturated solutions at $pH = 3-4$	Assuming that $f(H_2)$ is fixed by the H <sub>2</sub> S-S(s) equilibrium, logK of the reaction Au + H <sub>2</sub> S + HS <sup>-</sup> = Au(HS) <sub>2</sub> <sup>-</sup> +

 $0.5H_2$  are determined

1994	Pan & Wood	200-350	svp	Solubility of Au in $H_2O + NaOH(0.01-2 m) + Na_2SO_4(0.02-0.1 m) + H_2S(0.3-2.1 m)$ solutions	$\begin{array}{l} \text{logK of the reaction } Au + H_2S + HS^- = \\ Au(HS)_2^- + 0.5H_2 \end{array}$
1995	Gammons & Williams-Jones	300	svp	Solubility of Au–Ag alloys ( $X_{Au} = 0.3-1$ ) and AgCl <sub>(s)</sub> in 3 m HCl	Equilibrium composition of Au-Ag alloys and logK of the reaction $Au + 2Cl^- + H^+ = AuCl_2^- + 0.5H_2$
1995	Zotov & Baranova	23 & 80	1-500	Solubility of Au <sub>2</sub> S (23 $^{\circ}$ C) and AuAgS (80 $^{\circ}$ C) in near-neutral sulphide solutions	$V_{298}^{\circ}(\text{Au}(\text{HS})_{2}^{-})$
1996	Benning & Seward	150-500	500-1500	Solubility of Au in aqueous solutions: (a) $H_2S(0.02-0.1 \text{ m } S_{tot}) + H_2(0.035 \text{ bar}),$ (b) $H_2S(0.01-0.1 \text{ m } S_{tot}) + H_3PO_4(0.001-0.14 \text{ m}) + H_2(0.035 \text{ bar}),$ (c) $H_2S(0.02-0.11 \text{ m } S_{tot}) + NaOH(0.002-0.04 \text{ m}) + H_2(0.035 \text{ bar})$	Stability constants of Au(HS) <sup>0</sup> and Au(HS) <sub>2</sub> <sup>-</sup>
1997	Gammons et al.	100-200	svp	Disproportionation of $AuCl_2^-$ into Au and $AuCl_4^-$ in HCl solutions $(0.02-2 \text{ m})$	logK of the reaction: $3AuCl_2^- = 2Au + AuCl_4^- + 2Cl^-$
1998	Baranova & Zotov	300-350	500	Solubility of Au in H <sub>2</sub> O, HCl $(0.0002-0.2 \text{ m})$ and NaOH $(0.05 \text{ m})$ with H <sub>2</sub> S $(0.1 \text{ m})$ and H <sub>2</sub> (46-105 bar)	Stability constants of Au(HS) and Au(HS) <sub>2</sub>
1998	Gibert et al.	350-450	500	Solubility of Au in 0.5 m KCl solutions at QMF and PyPoMt or PyMtHe buffers	Reported stability constants of Au(HS) <sup>0</sup> are in agreement with the data of Hayashi & Ohmoto (1991) when recalculated to the AuHS stoichiometry
1999	Loucks & Mavrogenes	550-725	1000-4000	Synthetic fluid inclusions method; solubility of Au in H <sub>2</sub> O-KCl-HCl fluids at QMF and PPM buffers	Very high solubility of gold (up to 1000 ppm). AuHS(H <sub>2</sub> S) <sub>3</sub> is suggested and its HKF parameters determined
2000	Fleet & Knipe	100-400	1500	Solubility of Au in H <sub>2</sub> O–MgS solutions at very high H <sub>2</sub> S concentrations (up to 20.3 m)	Stability constants of Au(HS) <sub>2</sub>
2000	Murphy <i>et al</i> .	25-250	svp, 850, 1500	Raman spectra of gold-chloride complexes	Linear Au(I)-chloride complexes AuCl <sub>2</sub> <sup>-</sup> , with a single Raman band at $\sim$ 326 cm <sup>-1</sup> at $T = 250$ °C
2003 <i>a</i>	Stefánsson & Seward	300-600	500-1500	Solubility of Au in H <sub>2</sub> O and NaOH (0–0.5 m) solutions with $10^{-8}$ – $10^{-6}$ m H <sub>2</sub> , using a flow-through reactor	logK of the reaction Au + $H_2O = AuOH^0 + 0.5H_2$
2003 <i>b</i>	Stefánsson & Seward	300-600	500-1800	Solubility of Au in $H_2O + H_2(4 \cdot 10^{-6} - 8 \cdot 10^{-4}m) + HCl(0-1.4 m) + NaOH(0-0.3 m) + NaCl(0-1 m)$ solutions using in flow-through system	logK of the reaction Au + 2Cl <sup>-</sup> + H <sup>+</sup> = AuCl <sub>2</sub> <sup>-</sup> + 0.5H <sub>2</sub>

(Continued)

Table 3. Continued

Year	Authors	T, °C	P, bar	System composition	Main results
2004	Stefánsson & Seward	100-500	500	Solubility of Au in $H_2O + H_2 (1.6 \cdot 10^{-5} - 5.4 \cdot 10^{-4}m) + \sum S(0.016 - 0.133 m) + HCl(0 - 0.24 m) + NaOH(0 - 0.2 m) solutions in a flow-through system$	Stability constants of Au(HS) and Au(HS) <sub>2</sub> <sup>-</sup>
2004	Dadze & Kashirtseva	200-350	svp, 300, 1000	Solubility of Au in H <sub>2</sub> S-solutions: (a) thioacetamide $(0.05-0.5 \text{ m})$ + NaOH $(pH_{in} = 7.4-9)$ or HCl $(pH_{25^{\circ}C} = 1.44)$ , (b) thioacetamide $(0.05-0.5 \text{ m})$ + NaOH $(pH_{25^{\circ}C} = 7.4)$ + Na <sub>2</sub> SO <sub>4</sub> $(0.05 \text{ m})$	Stability constants of Au(HS) and Au(HS) <sub>2</sub> <sup>-</sup>
2005	Tagirov et al.	350-500	500-1000	Solubility of Au in KCl(0.001–0.1 m) solutions at OMF or OMA and PPM buffers	Stability constants of Au(HS) and Au(HS) $_2^-$
2006	Tagirov <i>et al.</i>	25-250	svp	Solubility of Au, Ag <sub>2</sub> S + Ag <sub>3</sub> AuS <sub>2</sub> and Ag <sub>3</sub> AuS <sub>2</sub> + AgAuS (25 °C), and AgAuS (91–250 °C) in sulphide solutions (0.012– 0.12 mS)	Stability constants of Au(HS) <sub>2</sub> <sup>-</sup>
2009 <i>a</i>	Pokrovski <i>et al.</i>	25-500	600	Stability and structure of Au <sup>I</sup> and Au <sup>III</sup> chloride complexes in Au–NaCl–HCl–AuCl <sub>4</sub> <sup>-</sup> aqueous solutions (pH $< 2$ ) using <i>in situ</i> XAS spectroscopy	AuCl <sub>4</sub> <sup>-</sup> is unstable upon heating and is rapidly transformed to Au <sub>(s)</sub> and AuCl <sub>2</sub> <sup>-</sup> . In the latter complex, Au is linearly coordinated by 2Cl atoms at an average distance of 2.27 Å.
2009 <i>b</i>	Pokrovski <i>et al.</i>	200-450	300-600	Au solubility and local structure in (a) S– NaOH, pH = 5–8, (b) $H_2O-S(\pm H_2SO_4)$ , pH = 2–4, (c) $H_2O-S-Na_2SO_4$ , pH = 4–5 aqueous solutions using <i>in situ</i> XAS spectroscopy	First <i>in situ</i> measurement of Au–S species structures at elevated $T-P$ . In all systems, Au is linearly coordinated by 2S atoms at 2.29 Å. Au(HS) <sub>2</sub> <sup>-</sup> dominates at pH > 6, but at pH <4-5, Au(HS)(H <sub>2</sub> S) and/or Au(HS)SO <sub>2</sub> are tentatively suggested, and their stability constants reported.

svp, saturated vapour pressure of the aqueous solution; PPM, pyrite-pyrrhotite-magnetite; PMH, pyrite-magnetite; PMH, pyrite-magnetite; MH, magnetite-hematite; QMF, quartz-muscovite-K feldspar; QMA, quartz-muscovite-andalusite; *m*, molality (number of moles of solute per 1 kg of water); I, ionic strength.

Thermodynamic model. The thermodynamic properties and stabilities of aqueous ions and complexes in hydrothermal fluids at elevated temperatures and pressures are successfully described using the Helgeson-Kirkham-Flowers (HKF) equation of state (Helgeson et al. 1981; Tanger & Helgeson 1988, Shock et al. 1989, 1997; Sverjensky et al. 1997). The HKF model has been demonstrated to be very versatile, being able to reproduce experimental stability constants of aqueous species and mineral solubilities in the liquid phase and dense supercritical fluid (density  $> \sim 0.3 - 0.5 \text{ g/cm}^3$ ) at temperatures from 0 °C to 1000 °C and pressures at or above the vapour-liquid saturation curve (P<sub>sat</sub>) to 10 kbar (e.g. Sverjensky *et al.* 1997; Pokrovski & Dubrovinsky 2011).

According to this model, any thermodynamic property of an aqueous species is regarded as a sum of solvation and non-solvation (or structural) contributions (see Oelkers et al. 2009 for a recent review). The former accounts for the interactions of the species with the solvent molecules, whereas the latter stems from the chemical bonding and molecular structure of the species itself. The solvation term is treated using the electrostatic Born (1920) equation, in which the so-called Born parameter  $(\omega)$  of an ion is defined by its crystallographic radius (Tanger & Helgeson 1988), whereas for an aqueous complex, composed of different ions, empirical correlations between the entropy and the Born parameter are used (Shock & Helgeson 1988). The non-solvation term is described by a series of empirical equations with four adjustable parameters accounting for the species non-solvation volume  $(a_1, a_2, a_3, a_4)$  and two adjustable parameters accounting for the species heat capacity  $(c_1 \text{ and } c_2)$ . To reduce the number of adjustable terms, the authors of the model proposed a series of empirical correlations amongst S, V,  $C_p$  at standard state conditions (25 °C, 1 bar) and  $a_{1-4}$  and  $c_{1,2}$  coefficients, depending on the species charge and based on a few aqueous species for which thermodymanic properties were available in a wide T-P range. These correlations were updated with the appearence of new experimental data, particularly for some neutral gases and complexes for which direct calorimetric  $(C_p)$  and volumetric (V) measurements at elevated temperatures have become available in the last 15 years, allowing a far more precise refinement of  $\omega$  and  $a_{1-4}$  and  $c_{1,2}$ coefficients (e.g. Schulte et al. 2001; Perfetti et al. 2008; Oelkers et al. 2009; references therein). These studies demonstrated that even neutral species have Born coefficients somewhat different from zero, in contrast to the classical Born equation that implies a zero  $\omega$  value for an uncharged species. However, these deviations from zero are small compared to  $\omega$  values for charged ions and,

for most mineral-fluid modelling purposes, may be ignored.

Thus, to describe the thermodynamic properties of an aqueous component, one should specify its standard Gibbs free energy of formation and entropy at 25 °C, 1 bar ( $\Delta_f G^{\circ}_{298}$  and  $S^{\circ}_{298}$ ), and seven temperature- and pressure-independent parameters for the solvation part (Born parameter  $\omega$ ). molar volume  $(a_1, a_2, a_3, a_4)$ , and heat capacity  $(c_1, c_2)$ . If data at different T and P are available for the stability constant of an aqueous complex (i.e. Gibbs free energy) or as direct measurements of  $C_p$  and V for a neutral species, its HKF parameters may be refined by adjusting them to match the measured stability constants and using additional contraints from interparameter correlations. For this purpose, the OptimB computer code (Shvarov 2010) has been used in the recent studies (Akinfiev & Zotov 2010; Tagirov et al. 2013), allowing user-friendly and statistically robust HKF parameter retrieval.

In the absence of reliable experimental high T-P data, the method of isocoulombic reactions may be applied (Jackson & Helgeson 1985). It has been demonstrated by a number of studies (e.g. Mesmer *et al.* 1988; Ruaya 1988) that, for an exchange reaction between aqueous species such as

$$AX_n^m + BY_k^l = BX_n^m + AY_k^l \tag{1}$$

where A and B denote metals and X and Y ligands with their corresponding charges (m, l) and stoichiometric coefficients (k, n), temperature and pressure dependences of the equilibrium constant of reaction (1) can be calculated, assuming no change in the heat capacity  $(\Delta_r C_p \approx 0)$  and molar volume  $(\Delta_r V \approx 0)$  of the reaction. This approach was successfully employed in recent papers reporting HKF parameters (Akinfiev & Zotov 2001, 2010; Akinfiev & Tagirov 2006; Akinfiev *et al.* 2006) and was used for some Au species as detailed below.

An important issue that determines the derivation of HKF parameters from experimental Au solubility studies is the thermodynamic properties of the major fluid constituents. These properties for pure solid phases, pure gases (H<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>S), 'simple' ions (Na<sup>+</sup>, Cl<sup>-</sup>, HS<sup>-</sup>, and OH<sup>-</sup>), and ion pairs (NaCl<sup>0</sup> and NaOH<sup>0</sup>) were taken from the SUPCRT92 thermodynamic database (Johnson *et al.* 1992) and its later extensions (Shock *et al.* 1997; Sverjensky *et al.* 1997; http://geopig3.la. asu.edu:8080/GEOPIG/index.html) without any revision or adjustment, both because they are judged to be reliable since based on a large experimental data set, and in order to maintain the internal consistency. The stability constant of NaHS<sup>0</sup> was assumed to be equal to that of NaCl<sup>0</sup>, because

of similar ion radii and charges of Cl<sup>-</sup> and HS<sup>-</sup>. The HKF parameters of HCl<sup>0</sup> were adopted from Tagirov et al. (1997). Thermodynamic properties of aqueous hydrogen sulphide  $H_2S^0(aq)$  and other dissolved gaseous species were calculated using the equation of state (EoS) of Akinfiev & Diamond (2003) proposed for aqueous non-electrolytes. This EoS allows avoiding uncertainties inherent in the HKF model when predicting thermodynamic properties of dissolved gases in water in near- and supercritical regions (Plyasunov & Shock 2001). It should be noted that the HKF-based dataset for  $H_2S^0(aq)$ (Schulte et al. 2001) yields values of Gibbs free energy of aqueous H<sub>2</sub>S similar to those of the Akinfiev & Diamond (2003) model within 2 kJ/ mol up to 500 °C. The model coefficients for the dissolved gases are provided in Table 4. A brief summary of the optimization results from recent studies (Akinfiev & Zotov 2001, 2010) for Au aqueous chloride, hydrogen sulphide, and hydroxide species is given below. The important feature of these compilations is that they used the original experimental solubility data points (where available) rather than final stability constants reported in the different experimental studies.

#### Optimization results and recommended thermodynamic properties of Au aqueous complexes

 $AuCl_2^-$ . The available experimental studies reporting the thermodynamic properties of the Au<sup>I</sup> dichloride complex embrace a wide range of temperatures (25–500 °C) and pressures (1–1500 bar) (Nikolaeva *et al.* 1972; Gammons & Williams-Jones 1995; Zotov *et al.* 1995). Original experimental data from these studies were recalculated to obtain Gibbs free energies of AuCl<sub>2</sub><sup>-</sup> at the temperatures and pressures of these experiments ( $g_{T,P}^{\circ}$ ). The obtained values of  $g_{T,P}^{\circ}$  were then used to optimize values of  $\Delta_f G_{298}^{\circ}$ ,  $S_{298}^{\circ}$ ,  $C_{p,298}^{\circ}$ , and  $\omega$  of this complex by the OptimB computer code (Shvarov 2010). The value of the standard molal volume of AuCl<sub>2</sub><sup>-</sup> was estimated from the isocoulombic reaction

$$\operatorname{Au}(\operatorname{HS})_{2}^{-} + \operatorname{AgCl}_{2}^{-} = \operatorname{AuCl}_{2}^{-} + \operatorname{Ag}(\operatorname{HS})_{2}^{-} \quad (2)$$

and using the corresponding values of  $AgCl_2^-$  and  $Ag(HS)_2^-$  from Akinfiev & Zotov (2001) and those of  $Au(HS)_2^-$  as derived below. The stability constants of  $AuCl_2^-$  reported by Stefánsson & Seward (2003*b*) are in good agreement with the present estimations above 450 °C, but by 1 log unit lower at 400 °C. Figure 1 shows the optimization results in terms of the difference in Gibbs energy values  $(g_{T,P}^-$  for  $AuCl_2^-)$  between the model and experimental datapoints for each original study as a function of temperature.

AuHS<sup>0</sup>. A similar optimization procedure was used to process available experimental data of Gibert et al. (1998), Baranova & Zotov (1998), Stefánsson & Seward (2004), and Tagirov et al. (2005, 2006). The data of Hayashi & Ohmoto (1991) reporting Au solubility in sulphide- and sulphate-bearing solutions have been recalculated to the AuHS stoichiometry. The data of Benning & Seward (1996) were excluded because they are inconsistent with more recent values reported by the same group (Stefánsson & Seward 2004), as well as by Tagirov et al. (2005, 2006). The Gibbs free energy value of AuHS<sup>0</sup> at 25 °C and 1 bar has been determined by Tagirov et al. (2006) to a high degree of accuracy ( $\pm 0.4 \text{ kJ/mol}$ ). The standard values of heat capacity and volume were estimated from the isocoulombic reaction

$$AuCl_2^- + AgHS^0 = AuHS^0 + AgCl_2^-$$
(3)

Species	$\Delta_f G_g^\circ {}_{298} \ \mathrm{cal} \cdot \mathrm{mol}^{-1}$	Ę	$cm^3 \cdot g^{-1}$	$cm^{3} \cdot K^{0.5} \cdot g^{-1}$	$\Delta_f G^\circ_{aq298} \ \mathrm{cal} \cdot \mathrm{mol}^{-1}$	$\operatorname{cal}\cdot\operatorname{mol}^{S_{298}^\circ}\mathrm{K}^{-1}$	$cm^{3} \cdot mol^{-1}$	$\operatorname{cal}^{C_{p,\ 298}^\circ}_{\operatorname{cal}\operatorname{mol}^{-1}\operatorname{K}^{-1}}$
H <sub>2</sub>	0	0.3090	- 8.4596	10.8301	4240	13.42	25.55	43.25
02	0	0.0600	-9.7540	12.9411	3966	26.86	33.23	52.66
H <sub>2</sub> S	-8021	-0.2017	-12.8031	13.5396	-6652	28.92	34.90	52.63
CÕ <sub>2</sub>	-94254	-0.085	-8.8321	11.2684	-92256	28.47	32.71	50.35
$CH_4$	-12122	-0.1131	-11.8462	14.8615	$-8196^{\circ}$	21.55	37.18	59.63
SO <sub>2</sub>	-71 723	-0.4234	-14.1409	14.1959	-71 840	37.79	38.51	56.32

 Table 4. Thermodynamic parameters of the Akinfiev & Diamond (2003) equation of state for gas-like neutral species in aqueous solution

The Gibbs function  $g_{aq}^{0}(P, T)$  of an aqueous non-electrolyte at given temperature T(K) and pressure P(bar) in the framework of this EoS is expressed as  $g_{aq}^{0}(P, T) = g_{g}^{0}(T) - RT \ln N_{w} + (1 - \xi)RT \ln f_{1}^{0} + RT \xi \ln \left(\frac{\tilde{R}T}{M_{w}}\rho_{1}^{0}\right) + RT \rho_{1}^{0} \left[a + b\left(\frac{10^{3}}{T}\right)^{0.5}\right],$ 

where  $g_{0}^{o}(T)$  stands for the Gibbs function of the corresponding species in the ideal gas state,  $M_{w} = 18.0152 \text{ g mol}^{-1}$ ,  $N_{w} = 1000/M_{w}$  mol,  $f_{1}^{o}$  and  $\rho_{5}^{b}$  are, respectively, the fugacity (in bars) and density (in  $g \cdot cm^{-3}$ ) of pure solvent (H<sub>2</sub>O) at given T and P, R = 1.9872 cal  $\cdot$  mol<sup>-1</sup>  $\cdot$  K<sup>-1</sup> and  $\tilde{R} = 83.144 \text{ cm}^{3} \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  are the ideal gas constants, and  $\xi$ , a, and b denote empirical coefficients for each species in the table. The data for aqueous species in the table ( $\Delta_f G_{aq298}^{o}, S_{298}^{o}, V_{298}^{o}$ , and  $C_{p, 298}^{o}$ ) were computed using this EoS. GOLD SPECIATION IN GEOLOGICAL FLUIDS



**Fig. 1.** Differences in the Gibbs free energy of the indicated Au aqueous species between experimental values derived from original studies (see section "Gold chloride, hydrogensulphide, and hydroxide species in aqueous solution and dense supercritical fluid" and Table 3) and calculated values using the recommended HKF parameters from Table 5 (see text for details).

and using the corresponding values of  $AuCl_2^$ derived above and those of  $AgHS^0$  and  $AgCl_2^$ from Akinfiev & Zotov (2001). It can be seen in Figure 1 that while the maximum deviations in  $g_{T,P}^\circ$  for AuHS do not exceed 1–2 kcal/mol, the trends with increasing temperature of Gibert *et al.*'s (1998) and Stefánsson & Seward's (2004) data are different. The reasons of this remain unclear.

 $Au(HS)_2^-$ . The available experimental data on the stability of the Au<sup>I</sup> bis-hydrogen sulphide complex (Renders & Seward 1989; Shenberger &

Table 5. Standard thermodynamic properties (298.15 K and 1 bar) and HKF parameters of Au aqueous species recommended in this study

Species	$\Delta_{\!f}G_{298}^\circ*$	$\Delta_{\!f} H_{298}^{\circ} *$	$S^{\circ \dagger}_{298}$	$C^{\circ\dagger}_{\ p,298}$	$V^{\circ \ddagger}_{298}$	$a_1 \cdot 10^{\$}$	$a_2 \cdot 10^{-2}$ *	$a_3^{\parallel}$	$a_4 \cdot 10^{-4\P}$	$c_1^{\dagger}$	$c_2 \cdot 10^{-4}$	$\omega \cdot 10^{-5*}$
$AuCl_2^-$	-36 795	-46 664	47.16	-26.4	68.6	11.4774	20.2425	-2.2063	-3.6158	27.0677	-22.440	0.8623
AuHSaq	8344	13 193	50.86	1.8	56.5	9.4965	15.4057	-0.3052	-3.1459	-38.1356	19.6524	0.0
$Au(HS)_2^-$	3487	4703	77.46	3.3	75.1	12.3373	22.3421	3.0317	-3.7026	-53.6010	31.4030	0.7673
Au <sup>+</sup>	39 000	45 182	16.50	0.58	31.4	6.1161	7.1520	2.9389	-3.0747	7.7764	-2.9158	0.1390
Au(OH) <sub>2</sub> <sup>-</sup> AuCl <sub>aq</sub> AuOH <sub>aq</sub>	-66 553 -3184 -32 716	-94 664 -2077 -41 533	12.90 41.73 21.89	-33.1 -15.1 -11.1	24.6 53.1 32.4	5.4533 9.0294 6.1937	5.5338 14.2654 7.3415	3.5749 0.1430 2.8644	-3.0078 -3.3687 -3.0825	-5.5091 -2.6993 -3.0370	-9.7771 -6.1162 -3.9635	0.8465 0.0 0.0

$$\label{eq:calibration} \begin{split} & \stackrel{+}{}^{*} cal \cdot mol^{-1}. \\ & \stackrel{+}{}^{cal} \cdot mol^{-1}K^{-1}. \\ & \stackrel{+}{}^{*} cal^{-1} \cdot mol^{-1} \cdot bar^{-1}. \\ & \stackrel{+}{}^{*} cal \cdot K \cdot mol^{-1} \cdot bar^{-1}. \\ & \stackrel{+}{}^{*} cal \cdot K \cdot mol^{-1}. \end{split}$$

Barnes 1989; Berndt et al. 1994; Zotov & Baranova 1995; Benning & Seward 1996; Baranova & Zotov 1998; Fleet & Knipe 2000) exhibit significant scatter; consequently, in the optimization we relied on the recent data of Stefánsson & Seward (2004) and Tagirov et al. (2005) reported in a wide T-Prange, together with low-temperature  $(25-150 \ ^{\circ}C)$ stability constants and the thermodynamic properties of Au<sub>2</sub>S(s) provided by Tagirov et al. (2006). The value of  $V_{298}^{\circ}$  for Au(HS)<sub>2</sub><sup>-</sup> was adopted as a mean of values reported by Benning & Seward (1996) and Baranova & Zotov (1998) based on pressure dependence of measured Au solubility, which is in agreement in both studies. At present, amongst all Au aqueous species, the stability of  $Au(HS)_2^{-}$  appears to be the best-constrained in a wide temperature (20-500 °C) and pressure (1-1000 bar) range (Fig. 1).

AuOH<sup>0</sup>. Experimental data on the hydroxide complex were reported by Zotov *et al.* (1995) in a limited *T* range (300–500 °C). Processing these data using the OptimB code yields  $\Delta_f G_{298}^\circ$  and  $S_{298}^\circ$  values, while  $C_{p,298}^\circ$ , and  $V_{298}^\circ$  were estimated using the isocoulombic reaction

$$AuCl_{2}^{-} + AgOH^{0} = AuOH^{0} + AgCl_{2}^{-}$$
(4)

with corresponding values of  $AgOH^0$  and  $AgCl_2^$ from Akinfiev & Zotov (2001) and of  $AuCl_2^-$  as derived above. Data of Stefánsson & Seward (2003*a*), not used in the optimization, are in agreement with our predictions within better than 0.5 log units in terms of AuOH<sup>0</sup> concentration.

 $AuCl^{0}$ ,  $Au^{+}$ ,  $Au(OH)_{2}^{-}$ . The thermodynamic properties of these species are poorly known, and their formation constants have only been estimated at ambient conditions. The  $\Delta_{f}G^{\circ}_{298}$  value of  $Au(OH)_{2}^{-}$  was obtained from the estimate of Peshchevitskii *et al.* (1976) for the reaction

$$AuCl_{2}^{-} + 2OH^{-} = Au(OH)_{2}^{-} + 2Cl^{-}$$
 (5)

A value of  $\Delta_f G^{\circ}_{298} = 39.0 \text{ kcal/mol for Au}^+$ was adopted from the SUPCRT92 database (Johnson *et al.* 1992; Shock *et al.* 1997), while its Born parameter was calculated using crystallographic ion radius  $R_{Au+} = 1.51 \text{ Å}$  (Huheey 1983). The  $\Delta_f G^{\circ}_{298}$  value of AuCl<sup>0</sup> was taken from Sverjensky *et al.* (1997). Other thermodynamic parameters for these species were estimated using the following isocoulombic reactions

$$\operatorname{AuCl}_{2}^{-} + \operatorname{Ag(OH)}_{2}^{-} = \operatorname{Au(OH)}_{2}^{-} + \operatorname{AgCl}_{2}^{-} \quad (6)$$

$$\operatorname{AuCl}_{2}^{-} + \operatorname{Ag}^{+} = \operatorname{Au}^{+} + \operatorname{AgCl}_{2}^{-}$$
(7)

$$AuCl_{2}^{-} + AgCl^{0} = AuCl^{0} + AgCl_{2}^{-}$$
(8)

and the corresponding *S*,  $C_p$ , and *V* values of Ag(OH)<sub>2</sub><sup>-</sup>, AgCl<sub>2</sub><sup>-</sup>, and Ag<sup>+</sup> from Akinfiev & Zotov (2001). The obtained thermodynamic properties of Au aqueous complexes are reported in Table 5, and the stability constants of the four main Au species (see reactions 10a to 10f below) are shown in Figure 2 as a function of temperature at 1 kbar pressure.

# The role of other sulphur-bearing forms in hydrothermal transport of gold

Other hydrogen sulphide complexes. The majority of available solubility experiments in H<sub>2</sub>Sdominated solutions overviewed above suggest the formation of monohydrogen sulphide species of presumed stoichiometry AuHS at acidic conditions, and of bis-hydrogen sulphide species,  $Au(HS)_2^{-1}$ at neutral-to-basic pH. The latter species has been recently confirmed by in situ XAS measurements of Au local structure and solubility in S-NaOH-H<sub>2</sub>O solutions (0.5–3 m S, pH  $\sim$ 5–8) from 200 to 450 °C (Pokrovski et al. 2009b). These experiments showed that Au is coordinated by two sulphur atoms in a linear geometry at Au-S average distances of 2.29  $\pm$  0.01 Å, and that the bulk solubility measured from the absorption edge height of the spectra (Figs 3 & 4) agrees within errors with



Fig. 2. Thermodynamic equilibrium constants of the formation reactions of the main Au chloride, hydroxide, and hydrogen sulphide complexes indicated in the figure as a function of temperature at 1000 bar according to the recommended HKF parameters in Table 5. Lines denote the reaction constants between metallic gold and the corresponding aqueous species from section "Major parameters controlling Au transport and precipitation in hydrothermal fluids" (reactions 10).



**Fig. 3.** Local structure of  $Au^{I}$  in sulphur-rich hydrothermal fluids revealed by *in situ* X-ray absorption spectroscopy (Pokrovski *et al.* 2009*b*). The left panel shows Fourier transform (FT) magnitudes of selected EXAFS spectra for neutral and acidic solutions of 0.5 m dissolved sulphur at 600 bar and indicated compositions and temperatures. Vertical dashed lines mark signals arising from the first S shell and from multiple scattering within the linear S-Au-S cluster. The right panel shows possible corresponding Au-S aqueous species whose structures and Au-S distances (in Å) were calculated using first-principles quantum chemistry. While the structural results at pH > 5 are consistent with Au(HS)<sup>2</sup><sub>2</sub>, spectra at acidic pH do not detect the AuHS complex inferred from available solubility data. By contrast, they indicate the formation of species containing two sulphur atoms like bis-hydrogen sulphide, mixed HS-SO<sub>2</sub>, polysulphide, or thiosulphate complexes. The insufficient knowledge of sulphur speciation itself and low spectral resolution of beyond-the-first atomic shells do not allow distinguishing between those species (see Pokrovski *et al.* 2009*b* for details).

the thermodynamic properties of  $Au(HS)_2^-$  recommended above from solubility measurements in hydrothermal reactors.

However, at acid conditions (in systems such as  $S-H_2O$ ,  $S-Na_2SO_4-H_2O$ , pH < 4-5), the XAS structural and solubility data of Pokrovski et al. (2009b) are inconsistent with the dominant formation of AuHS<sup>0</sup>. Their data reveal linear S-Au-S structures with Au-S distances of 2.29 Å, very similar to the experiments at neutral-to-basic pH, and solubilities of 1-2 orders of magnitude higher that those calculated using the thermodynamic properties of AuHS recommended above (Table 5). These findings were tentatively interpreted by Pokrovski et al. (2009b) by the formation of the neutral AuHS $(H_2S)^0$  complex. Such species was also suggested by Hayashi & Ohmoto (1991) from solubility measurements in similar solutions. Wood et al. (1987) also assumed this species to be dominant in acidic Cl-free solutions buffered with sulphide mineral assemblages. Other neutral Au species with H<sub>2</sub>S, such as tetrakis-hydrogen sulphide, AuHS( $H_2S$ )<sup>0</sup><sub>3</sub>, have been suggested by Loucks & Mavrogenes (1999) in high-temperature metamorphic fluids on the basis of Au solubility experiments in FeS-FeS2-silicate assemblages

at temperatures 500–700 °C and pressures 2– 4 kbars. However, this species was confirmed neither by XAS data of Pokrovski *et al.* (2009*b*) at lower T-P, nor by first-principles molecular dynamics simulations (MD) of Liu *et al.* (2011), who showed that this complex breaks down to AuHS(H<sub>2</sub>S) and two H<sub>2</sub>S molecules. In addition, the HKF parameters of the tetrakis-hydrogen sulphide complexes suggested by Loucks & Mavrogenes (1999) yield calculated solubilities of 1–2 orders of magnitude higher than those measured by XAS at temperatures below 450 °C (Fig. 4; see Pokrovski *et al.* 2009*b* for detailed discussion and comparison).

However, three limitations do not yet allow definitive conclusions as for the dominant presence of AuHS(H<sub>2</sub>S)<sup>0</sup> in acidic S-rich (H<sub>2</sub>S > 0.1 m) solutions: (1) The scatter of datapoints in the solubility studies discussed above makes it difficult to obtain unambiguous derivation of complex stoichiometry. (2) The intrinsically poor sensitivity of XAS to long distances, light neighbours (like H), and/or beyond-the-first shell neighbours around the absorbing atom does not allow definitive constraints on the complex stoichiometry beyond the [S-Au-S] cluster (Pokrovski *et al.* 2009*b*).

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**Fig. 4.** (a) Determination of the concentration of Au dissolved in the fluid phase can be done from the amplitude of the absorption edge height (see Pokrovski *et al.* 2005*b*, 2006, 2009*b* for details). (b) and (c) Evolution of Au molality, measured from the spectrum absorption edge height as a function of time in the presence of an excess of native gold in two experiments at neutral (b) and acidic (c) pH, shown in Figure 3 above. Each symbol corresponds to an XAS scan; arrows indicate temperature changes during the experiments; dashed horizontal lines (where present) denote the steady-state Au concentration at each temperature. Grey error bars stand for the range of Au dissolved concentrations in equilibrium with metallic gold as calculated using the stability constants of Au(HS)<sub>2</sub><sup>-</sup> and AuHS from available literature sources reviewed above. Double-end arrows in panel (c) represent the range of calculated Au concentrations using the stability constants of HayAshi & Ohmoto (1991) carried out in similar systems as those in the XAS experiments of Pokrovski *et al.* (2009*b*).

(3) Complex and poorly known sulphur speciation itself in the studied solutions does not allow exclusion of complexes with sulphur forms other than hydrogen sulphide. The following section discusses the possible role of such complexes.

Polysulphide and thiosulphate complexes. These ligands often form as intermediate reaction products in S-bearing solutions, in which sulphide and sulphate coexist, and during sulphur oxidation at low-to-moderate temperatures where meta-stable equilibria may occur both in nature and experiments (e.g. Ohmoto & Lasaga 1982). Both types of ligands have strong affinity for Au<sup>I</sup> (Table 2). The stability of  $Au(S_2O_3)_2^{3-}$  is comparable to that for  $Au(HS)_2^{-}$ at ambient conditions (log10K for both species  $\sim$ 26-30, see Table 2). According to Webster (1986), the thiosulphate complex may be responsible for gold remobilization during low-temperature oxidation of sulphide ores. For example, thiosulphate concentrations in some geothermal springs at  $T \le 100$  °C attain values comparable to those of H<sub>2</sub>S (Migdisov & Bychkov 1998; Xu et al. 1998) and thus may bind Au and similar metals

(e.g. Ag). Thiosulphate is, however, unstable at acidic pH below 100 °C, breaking down to native sulphur and sulphate (e.g. Kaasalainen & Stefánsson 2011).

Polysulphide Au complexes (AuS<sub>n</sub>S<sup>2-</sup>, where n = 2-7) were reported to form at moderate temperatures (100-150 °C) in Au solubility experiments in solutions saturated with elemental sulphur (Berndt et al. 1994); however, because of the complexity of the system containing comparable concentrations of different polysulphides and thiosulphate, no preference could be given to any Au species. Other solubility studies at 200-300 °C near the sulphate-sulphide equilibrium also evoked polysulphide and/or thiosulphate complexes to explain the elevated Au solubilities (Pal'yanova et al. 1993; Dadze & Kashirtseva 2004). These complexes were suggested to compete with hydrogen sulphide for Au during its transport in near-surface epithermal and active geothermal systems. Unfortunately, a quantitative estimation of the impact of such ligands on Au transport by hydrothermal fluids is greatly hampered by the lack of data on the stability and amounts of these sulphur forms at

above-ambient temperatures and pressures. Recent in situ experiments indicate that such forms may be stable in S-rich fluids at elevated temperatures. Pokrovski & Dubrovinsky (2011) and Pokrovski & Dubessy (2012), using in situ Raman spectroscopy in diamond-anvil and silica-capillary cells, showed that an unexpected sulphur species, the trisulphur radical ion  $S_3^-$ , forms rapidly and reversibly in sulphide-sulphate solutions between 250 °C and 500 °C and pH  $\ge 2-3$  in a wide range of pressures, from  $P_{\text{sat}}$  to 50 kbar. This trisulphur species, known by chemists since the 1970s to exist in a variety of ionic non-aqueous liquids, silicate glasses, alkalimetal sulphide batteries, alkali chloride melts, and ultramarine pigments (Chivers & Elder 2013), is now suggested to play a role in natural hydrothermal fluids. In particular, by analogy with 'classical' polysulphide forms ( $S_n S^{2^-}$ , see above), this species is expected to form stable complexes with Au<sup>I</sup> and thus may probably account, at least partly, for the Au elevated solubilities obtained by Hayashi & Ohmoto (1991), Loucks & Mavrogenes (1999) and Pokrovski et al. (2009a). Detailed account of the role of this new sulphur form in Au transport by natural hydrothermal fluids requires accurate knowledge of the  $S_3^-$  stability domain and specially designed spectroscopic and solubility experiments on Au within this domain.

Sulphur dioxide and sulphites. Another important sulphur ligand that might impact gold transport in high-T magmatic-hydrothermal fluids is sulphite  $(SO_2, and its dissociation products, HSO_3^- and$  $SO_3^{2-}$ ). This sulphur form is particularly abundant at acidic pH and temperatures above 400 °C under oxidizing conditions typical of porphyry Cu-Au deposit formation (Kouzmanov & Pokrovski 2012). Note that the stabilities of Au<sup>I</sup> sulphite and thiosulphate complexes at ambient conditions are similar (Table 2). Gold-sulphite or -SO<sub>2</sub> species may equally account for the observed Au twofold S coordination and elevated solubilities compared with AuHS<sup>0</sup> in Pokrovski et al.'s (2009b) experiments. Because metal-ligand interactions generally become 'harder' with increasing temperature, following the decrease of the solvent dielectric constant and thus reinforcement of coulombic attractions (e.g. Crerar et al. 1985; Brimhall & Crerar 1987), high-temperature conditions might be beneficial for Au complexing with SO<sub>2</sub>, which is a 'harder' ligand than H<sub>2</sub>S. The formation of Au-SO<sub>2</sub> species is thus expected to be favoured in magmatic fluids typical of active convergent margins where SO<sub>2</sub> often largely dominates over H<sub>2</sub>S (e.g. Borisova et al. 2006; references therein). The geological spatial and temporal links, widely documented in these areas between magmatic plutons and overlaying epithermal high sulphidation

Au-Cu deposits, are often interpreted by the transport of Au and Cu by oxidizing, acidic magmatic fluid or vapour phases enriched in SO<sub>2</sub> (e.g. Hedenquist & Lowenstern 1994; Hedenquist et al. 1998; Heinrich 2007; Pokrovski et al. 2008a). No direct data exist on Au complexing by SO<sub>2</sub> for magmatic fluids; however, Zajacz et al. (2010, 2011) reported variable Au metal solubility from a few ppm to 100s ppm in aqueous SO<sub>2</sub>-dominated NaCl-bearing fluids at 1000 °C and 1.5 kbar from synthetic fluid inclusion experiments at oxidizing conditions (up to  $\sim$ NNO + 2.0). Although these Au concentrations are lower than those measured in H<sub>2</sub>S-dominated fluids (NNO - 0.4) of similar total salt and sulphur content from those studies, sulphur speciation in these systems is insufficiently constrained since it was based on calculations using thermodynamic properties of ideal gas species  $H_2S(g)$  and  $SO_2(g)$ . Thus, as for other sulphur species of intermediate valences, the major obstacle in quantifying the contribution of SO<sub>2</sub> in Au transport is the paucity of high T-P thermodynamic and PVTX data for S<sup>IV</sup> aqueous species and their partitioning between vapour, brine, and silicate melt. One of the major near-future research challenges on magmatichydrothermal systems will be to assess the identity and amounts of the different complexes formed by sulphur in aqueous fluid, vapour phase, and silicate melt, in particular using in situ spectroscopic methods, both in model laboratory systems and natural fluid/melt inclusions.

# Vapour transport and vapour-liquid partitioning of gold

One of the major last-decade advances in understanding magmatic-hydrothermal systems, particularly those hosting porphyry Au-Cu-Mo and associated epithermal Au-Cu deposits, is the recognition that the vapour phase can transport significant quantities of metals including Au (Heinrich et al. 1992, 1999, 2004; Audétat et al. 1998; Ulrich et al. 1999). This has motivated experimental and theoretical research that allowed new constraints on the physical and chemical factors affecting the vapour-phase transport and vapour-brine partitioning of Au and associated metals. These factors are discussed in this section with a particular emphasis on Au, whereas other metals are briefly mentioned for comparison; they have been a subject of more detailed recent reviews (e.g. Williams-Jones & Heinrich 2005; Simon & Ripley 2011; Kouzmanov & Pokrovski 2012).

Lessons from volcanic gases and natural fluid inclusions. Extensive work on volcanic gases and fumarole condensates and sublimates since the mid-20th century suggests selective vapour transport of

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many metals (Symonds et al. 1987, Symonds & Reed 1993; Hedenquist et al. 1994; Taran et al. 1995, 2001; Pokrovski et al. 2002a). Despite large variations in a few cases, the majority of volcanic gas and fumarole vapour samples show mean metal concentrations typically of a few ppm for many economic metals (Zn, Pb, Cu, Sn, Mo, Ag, As). By contrast with most metals and metalloids. for which large databases on their sublimation mineralogy and fumaroles contents are available from many active volcanoes all over the world (e.g. Williams-Jones & Heinrich 2005; references therein), only a few studies report findings of Au as native metal or Cu-Ag-Au alloys in sublimates collected on active volcanoes such as La Fossa, Italy (Filignati & Sbrana 1998), Colima, Mexico (Taran et al. 2000), and Kudryavy, Kurile Islands (Yudovskaya et al. 2006). The reported analyses of Au in fumarole vapour condensates are scarce and exhibit large variations, which reflect both the difficulties of accurate high-temperature sampling and imperfections of chemical treatments and analytical techniques for this poorly soluble trace metal. For example, Au contents reported in volcanic vapour condensates vary from  $\sim 0.001$  ppb (Hedenquist et al. 1994) to 5-20 ppb (Gemmel 1987; Ouisefit et al. 1989). More recent reports, from Colima and Kudryavy volcanos, however, systematically show Au concentrations in condensates less than 1 ppb (Taran et al. 2001; Yudovskaya et al. 2008; Chaplygin 2010), which are comparable with Au contents in unaltered volcanic rocks from these areas (typically 0.1-1 ppb, Taran et al. 2001) and are somewhat lower than the Au mean crustal abundance (1-2 ppb).

Gas phase transport and precipitation of many metals and metalloids have been the subject of extensive thermodynamic modelling based on gassublimate chemical equilibria in water-free systems (e.g. Symonds et al. 1987, 1992; Symonds & Reed 1993; Tkachenko et al. 1999; Churakov et al. 2000; Pokrovski et al. 2002a; references therein) and using chloride, sulphide, oxide/hydroxide, or native metal gaseous species whose thermodynamic properties are available in large databases (e.g. JANAF - Chase 1998; Ivtanthermo - Belov et al. 1999; GASTHERM - Symonds & Reed 1993). In contrast, limited modelling was devoted to Au, mostly because of the lack of data on its gaseous species. Gold gaseous species are not reported in those databases, and the available data are limited to Au, AuH, and AuS from the compilations of Pankratz et al. (1987), Pankratz (1982), and Barin (1995). To the best of our knowledge, the only studies that attempted to thermodynamically model Au volcanic gas chemistry are those of Taran et al. (2000, 2001). These authors used the above thermodynamic data to estimate Au transport and

precipitation by Colima volcanic gases and found qualitative agreement between the Au distribution observed in sampling silica tubes and their thermodynamic predictions. Other Au gas species, mostly explored by chemists in the 1970s, under HClrich highly oxidizing conditions include  $Au_2Cl_2(g)$ and Au<sub>2</sub>Cl<sub>6</sub>(g) (Hager & Hill 1970; Landsberg & Hoatson 1970: James & Hager 1978: Tagirov et al. 1993). However, the formation of such polymeric species requires Au concentrations much higher than those in volcanic gases; it is also unlikely that Au<sup>III</sup> chloride complexes would be stable in natural volcanic systems where Au<sup>I</sup> is expected to be the dominant gold redox state (see section 'General features of gold aqueous chemistry'). It is clear that quantitative modelling of Au transport by volcanic gases awaits accurate thermodynamic data for key Au gaseous species, such as hydroxides, chlorides, and sulphides.

The gold contents of the volcanic gas phase both measured and modeled thermodynamically are, however, 2-5 orders of magnitude lower than those measured over the last decade in vapour-like inclusions from magmatic-hydrothermal deposits (Heinrich et al. 1999; Ulrich et al. 1999, 2001; Audétat & Pettke 2003; Kehayov et al. 2003; Baker et al. 2004; Williams-Jones & Heinrich 2005; Klemm et al. 2007, 2008; Seo et al. 2009, 2012). These inclusions, together with their high-salinity liquid counterparts, trapped in guartz and other minerals during their growth from hydrothermal fluids, record vapour-liquid phase immiscibility events that a saline metal- and volatile-bearing magmatic fluid undergoes upon its cooling and decompression when rising to the surface (Hedenquist & Lowenstern 1994; Heinrich et al. 1999; Kouzmanov & Pokrovski 2012; references therein). These events result in the formation of assemblages of syngenetic inclusions of low-salinity aqueous vapour (typically  $<\sim 10$  wt% NaCl equiv, density  $\sim 0.01-0.3$  g/ cm<sup>3</sup>) and hypersaline liquid (typically  $\sim 20-80\%$ NaCl equiv., density  $>0.5-0.6 \text{ g/cm}^3$ ), produced by fluid unmixing. Metal partitioning between these two phases is found to be in sharp contrast. Most base, alkali, and alkali earth metals (Na, K, Sr, Fe, Zn, Pb) are preferentially enriched in the liquid, with vap/liq partitioning coefficients  $K_{\rm vap/lig}$  typically less than 0.1, whereas Cu and Au  $(\pm As, \pm Mo)$  show a significantly stronger preference for the vapour phase, with  $K_{\text{vapour/liquid}}$ values from 0.1 to 100 (see compilation of Kouzmanov & Pokrovski 2012 and Fig. 5). Among these metals, Au exhibits the highest K values, attaining almost 100 in favour of the vapour phase (Fig. 5), with absolute Au concentrations as high as 10 ppm (see also section 'Comparison of thermodynamic predictions with natural data from porphyry Cu-Au-Mo and related deposits' and Fig. 12 below).



**Fig. 5.** Concentration ratios (equivalent to vapour-liquid partition coefficient,  $K = C_{vapour}/C_{liquid}$ ) for sulphur, gold, and associated metals measured in coexisting vapour and hypersaline liquid inclusions from boiling assemblages in quartz from porphyry Cu–Au–Mo and related deposits, obtained by *in situ* laser ablation ICPMS (modified from Kouzmanov & Pokrovski 2012). Data are from Heinrich *et al.* (1999), Ulrich *et al.* (1999, 2001), Audétat & Pettke (2003), Kehayov *et al.* (2003), Baker *et al.* (2004), Williams-Jones & Heinrich (2005), Klemm *et al.* (2007, 2008), and Seo *et al.* (2009, 2012). Note that the enhanced partitioning of Cu into the vapour phase (*K* up to 100) is likely to be a post-entrapment artifact due to Cu diffusion through quartz (see text and Lerchbaumer & Audétat 2012 for details).

Such Au concentrations cannot be explained by the available data on Au gas species in dry systems discussed above that yield ppb levels of Au in H<sub>2</sub>S-HCl aqueous vapour saturated with the metal. The main difference between near-surface volcanic gases and hydrothermal vapours is the density, which increases by a factor of 100 from the surface ( $d_{vap} \approx 0.001 \text{ g/cm}^3$  at <10 bar) to a few km of depth ( $d_{vap} \approx 0.01-0.4 \text{ g/cm}^3$  at 100– 1000 bar). Vapour density thus appears to be the major parameter affecting gold and other minerals solubility in the vapour-phase domain, as will be shown below.

Solvation control on Au solubility in vapour. Recent solubility studies of Au and CuCl, AgCl, SnO<sub>2</sub>, and MoO<sub>3</sub> solids in unsaturated water vapour (i.e. at pressures below the vapour-liquid saturation curve of water or H<sub>2</sub>O-salt solution,  $P_{sat}$ ) have confirmed that the dominant control on metal solubility is water pressure (Williams-Jones & Heinrich 2005; Rempel *et al.* 2009; and references therein). They show that at water pressures of a few hundred bars and temperatures of 200–400 °C, the solubility of a solid oxide, chloride, or native metal is many orders of magnitude higher, compared to the volatility of this solid in a  $H_2O$ -free system. More detailed overviews of Cu, Ag, Sn, and Mo solubility in these systems can be found elsewhere (Williams-Jones & Heinrich 2005; Kouzmanov & Pokrovski 2012; Pokrovski *et al.* 2013*b*); here, we focus on the Au data.

Solubility experiments of native gold in undersaturated vapour of the HCl-H<sub>2</sub>O, H<sub>2</sub>S-S, and H<sub>2</sub>S-S-H<sub>2</sub>O systems were conducted by Archibald *et al.* (2001) and Zezin *et al.* (2007, 2011) at temperatures 300-360 °C and pressures below  $P_{sat}$ . These experiments showed enhanced volatility of Au in the presence of water, which was explained by the solid-gas reactions

$$Au(s) + HCl(gas) + mH_2O(gas)$$
  
= AuCl · mH\_2O(gas) + 0.5H\_2(gas) (9a)  
Au(s) + H\_2S(gas) + mH\_2O(gas)

$$= AuS \cdot mH_2O(gas) + H_2(gas)$$
(9b)

where *m* is the apparent hydration number, which depends on the species identity, temperature, and pressure. With increasing pressure, in the chloride system it systematically increases from 3 to 5 and, in the sulphide system, from 0 to  $\sim$ 2 in the *T*–*P* range investigated. In H<sub>2</sub>O-poor experiments in the presence of large amounts of hydrogen sulphide gas (up to  $\sim$ 100 bar H<sub>2</sub>S), Au solubility was described by the solvation reaction

$$Au(s) + (n + 1)H_2S(gas)$$
  
= AuS \cdot nH\_2S(gas) + H\_2(gas) (9c)

where *n* is close to 2 (Zezin *et al.* 2007).

These studies reveal three fundamental controls on vapour-phase transport of gold: (1) In the aqueous vapour phase, Au forms complexes with the same ligands as in aqueous solution (chloride, sulphide, or water); however, Au ligation number and Au redox state might be different (see below). (2) In contrast to the aqueous solution or dense supercritical fluid, in which charged Au species dominate (AuCl<sub>2</sub><sup>-</sup>, Au(HS)<sub>2</sub><sup>-</sup>, see section, 'Gold chloride, hydrogen sulphide, and hydroxide species in aqueous solution and dense supercritical fluid'), the major vapour species are likely to be uncharged (at least in unsaturated vapour and moderate  $P_{H_2O}$ below the water critical point); this is in agreement with the low dielectric constant of the vapour favouring ion association. (3) As in aqueous solution, the gold complexes in the vapour are solvated by water molecules; the higher the pressure (or solvent density), the more metal can be dissolved in a vapour-solid system.

The main limitation of this hydration/solvation approach is a relatively narrow temperature and pressure range of available measurements and large changes in apparent hydration numbers with pressure for chloride species, which makes the practical application difficult at the wide T-Prange of hydrothermal gold deposit conditions. In addition, gold coordination number and valence state in S-bearing gaseous species suggested by these studies from analyses of bulk Au concentration dependence v. H<sub>2</sub>O and H<sub>2</sub>S fugacity remain poorly constrained. For example, reactions (9b, c) require Au redox state to be +2 and coordination number 3 in the species formed. This is in contradiction to both the dominant Au redox state of +1 and typical coordination numbers of 2 in fluids and minerals at hydrothermal conditions (see above). Gold solubility, calculated by Zezin et al. (2011) using the stability constants of reactions (9a, b), appears, however, to be less than 0.5 ppb Au in a typical hydrothermal vapour or liquid phase under porphyry-epithermal conditions  $(T \sim 350 \,^{\circ}\text{C}, P_{\text{H},\text{O}} \sim 100-400 \text{ bar}, \text{H}_2\text{S} \text{ concen-}$ trations  $\sim$  few wt% as found in natural fluid inclusions, e.g. Seo et al. 2009). This calculated Au concentration is many orders of magnitude lower than that measured in natural fluid inclusions from porphyry-epithermal Au-Cu deposits (100-10 000 ppb; Seo et al. 2009; Kouzmanov & Pokrovski 2012). These discrepancies imply that other species control gold transport in natural liquid-like fluids and vapours at these conditions. More work, combining solubility with in situ spectroscopic techniques and molecular modelling, is needed to better understand the chemical state and molecular structure of gold in hydrothermal vapour phases.

Fluid-density control on vapour-liquid partitioning of gold at hydrothermal conditions. Further insight into the vapour transport of gold and associated metals (As, Cu, Ag, Zn) has recently been offered by direct measurements of vapour-liquid partition coefficients of metals in model two-phase salt-water systems analogous to brine- and vapour-like fluid inclusions from porphyry Cu-Au deposits at temperatures from 300 °C to 500 °C and pressures from  $P_{\text{sat}}$  to ~500 bar (Pokrovski *et al.* 2005*a*, 2008*a*, *b*; Pokrovski 2010; references therein). These works demonstrate that the vapour-liquid distribution of elements obeys simple relationships involving the densities of the coexisting vapour and liquid phases. Figure 6 shows that, on a logarithmic scale, the partition coefficient of each metal ( $K_{vapour/liquid}$ , which is the ratio of metal mass concentrations in the coexisting phases,  $C_{\text{vapour}}/C_{\text{liquid}}$  is linearly proportional to the ratio between the vapour and liquid densities  $(d_{vapour}/d_{liquid})$ , which are wellknown in the H<sub>2</sub>O-NaCl system (e.g. Driesner &



Fig. 6. Vapour-liquid partition coefficients, log  $K_{\text{vapour/liquid}} = \log (m_{\text{vapour}}/m_{\text{liquid}})$ , where *m* is the number of moles of the element per 1 kg of fluid in the corresponding phase, of selected metals and metalloids at the two-phase equilibrium in the system  $H_2O + NaCl \pm KCl \pm HCl$  at temperatures between 250 and 450 °C as a function of the vapour-to-liquid density ratio. Symbols stand for experimental data from the following sources: As<sup>III</sup>, Cu<sup>I</sup>, Ag<sup>I</sup>, and Au<sup>I</sup>–Pokrovski *et al.* (2005*a*); Sb<sup>III</sup>–Pokrovski *et al.* (2005a, 2008b); La-Shmulovich et al. (2002). Na, Fe, and Zn (omitted for clarity) plot close to Cu (Pokrovski *et al.* 2005*a*). Limited data for Mo<sup>VI</sup> (Rempel *et al.* 2009) and Pb (Pokrovski et al. 2008a) plot close to As and Cu, respectively (omitted for clarity). Lines represent the regression through the origin (i.e. critical point, c.p.) of the experimental data for each element using the equation log  $K = n \times \log (d_{vapour}/d_{liquid})$ , where *n* is an empirical coefficient for each metal independent of temperature and salinity (Pokrovski et al. 2005a).

Heinrich 2007). All lines tend to converge to the critical point of the system where the concentrations are identical in both phases and the partition coefficient is, by definition, equal to one. Such 'ray diagrams' have long been known for partitioning of salts and acids between vapour and aqueous solution (e.g. Styrikovich et al. 1955; Alvarez et al. 1994); they stem from classical thermodynamics and statistical mechanics showing that the hydration energy of a solute evolves linearly with the solvent density (Mesmer et al. 1988; Anderson et al. 1991; Palmer et al. 2004). The relationships in Figure 6 confirm the validity of this model for a variety of metals and metalloids in a wide temperature range. They support the findings in unsaturated vapour systems (see above) and demonstrate that water-solute interaction (or hydration) is a key factor controlling metal vapour-phase solubility

and vapour-liquid partitioning. The following qualitative trend of element volatility in a two-phase water-salt system (in the order of decreasing  $K_{\text{vapour/liquid}}$  values) may be established:  $B \approx As^{\text{III}} > \text{Si} \approx \text{Sb}^{\text{III}} \approx Au^{\text{I}} > \text{Cu}^{\text{I}} \approx \text{Fe}^{\text{II}} \approx \text{Na} \approx$  $K \ge Zn > Ag \approx Cd \approx REE$  (Pokrovski 2010: Kouzmanov & Pokrovski 2012). Metalloids that form neutral hydroxide species both in the vapour and liquid are distinctly more volatile than most metals forming charged chloride complexes in the liquid phase. Gold that forms predominantly  $AuCl_{2}^{-}$  in the S-free liquid phase, according to available thermodynamic data discussed above (section "Gold chloride, hydrogensulphide, and hydroxide species in aqueous solution and dense supercritical fluid"), appears to be the most volatile metal investigated so far, as shown by the three available experimental datapoints (Fig. 6) obtained at 450 °C in the NaCl-HClH<sub>2</sub>O system in the presence of the Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> redox buffer (Pokrovski et al. 2005a). The exact nature and composition of Au species in the vapour phase remain unclear, and available data for AuCl  $\cdot$  mH<sub>2</sub>O(gas) (Archibald et al. 2001) do not allow reliable extrapolations above 350 °C. Whatever the exact species stoichiometry for Au and other metals in the vapour phase, it can be seen in Figure 6 that, contrary to As  $(\pm B, \pm Mo, \text{ not shown})$  whose  $K_{\text{vapour/liquid}}$ values approach one, gold and other metals are unable to enrich the vapour phase relative to the coexisting liquid. All of them are concentrated in the liquid by a factor of 10-1000 at conditions typical of vapour-brine separation in porphyry and related systems at temperatures to at least 500 °C.

Vapour-liquid partitioning of gold at magmatic conditions. At magmatic temperatures (600-800 °C), limited experimental data were obtained by the method of synthetic fluid inclusions trapped in quartz for Au, Cu, Zn, Ag, and Fe in sulphur-free systems, involving Na, K, and Fe chloride brines, silicate melts, and H<sub>2</sub>O-HCl vapour phases (see Simon & Ripley 2011; Kouzmanov & Pokrovski 2012 for reviews on different metals). Only two studies explored Au solubility and partitioning in S-free vapour-brine-melt systems of NaCl-KCl-FeCl<sub>2</sub>-H<sub>2</sub>O-haplogranite compositions at 800 °C, 1.0-1.5 kbar, and redox conditions buffered by the Ni-NiO assemblage (Frank et al. 2002; Simon et al. 2005). Data on Au solubility in melts and fluid/melt partitioning will be discussed in section "Gold speciation and solubility in magmatic fluids and fluid-melt partitioning." The solubility of Au in the acidic brine phase was tentatively interpreted as AuHCl<sub>2</sub><sup>0</sup>, while hydroxide species (e.g. AuOH<sup>0</sup>) were suggested to form at near-neutral low-HCl brine compositions. A third study of the same group (Frank et al. 2011) explored a similar

system at the same T-P-redox conditions but in the presence of iron sulphide assemblages to buffer sulphur fugacity.

The Au vapour-brine partitioning coefficients reported in these works are plotted in Figure 7. They also obey, despite the large data scatter, density relationships similar to those established for lower temperature hydrothermal conditions (shown by the red line labelled Au in this figure), although with absolute vapour-brine partition



log (density <sub>vapor</sub> / density <sub>liquid</sub>)

Fig. 7. Vapour-liquid partition coefficients  $\log K_{\text{vapour/liquid}} = \log (m_{\text{vapour}}/m_{\text{liquid}})$ , where m is the mass concentration of a metal per 1 kg of the vapour or liquid phase, of Au in two-phase model systems  $H_2O + NaCl \pm KCl \pm HCl \pm FeCl_2 \pm sulphur \pm$ pyrrhotite measured at hydrothermal (350-500 °C) and magmatic (800 °C) temperatures as a function of the vapour-to-liquid density ratio. Symbols stand for experimental data from the following sources: S05-Simon et al. (2005), F11-Frank et al. (2011), P08-Pokrovski et al. (2008a). Vertical error bars denote 1 standard deviation from the mean of multiple runs/analyses. For comparison, the straight lines through the critical point (c.p.) for the indicated elements represent the density-model predictions in the S-free system based on data below 500 °C (Fig. 6) from Pokrovski et al. (2005a). At magmatic temperatures and sulphur content of a few wt%, the effect of sulphur on Au vapour-liquid partitioning is weak in front of the large errors that affect the data. In contrast, at hydrothermal temperatures at acidic pH, Au partitions preferentially into the vapour,  $K_{\text{vapour/liquid}} \approx 1-10$ , whereas at neutral-to-basic pH, the effect of sulphur is much weaker, consistent with the change of Au liquid-phase speciation from neutral AuHS<sup>0</sup> and/or AuHSH<sub>2</sub>S<sup>0</sup> to negatively charged Au(HS)<sub>2</sub><sup>-</sup> at pH above  $\sim 5$  (see section "Gold chloride, hydrogen sulphide, and hydroxide species in aqueous solution and dense supercritical fluid").

coefficients ~0.5 order of magnitude higher on average than at  $T < \sim 500$  °C for similar vapour/ liquid density ratios (Fig. 6). Similar differences, not exceeding one unit of log  $K_{\text{vapour/liquid}}$ , were observed for Cu, Ag, Zn, and Fe. The increasing volatility of Au and these metals at magmatic conditions compared to hydrothermal temperatures might be explained by possible formation of hydroxide or hydrogen chloride species both in vapour and brine (e.g. AuOH, AuHCl<sub>2</sub>, Simon *et al.* 2005).

Both vapour and liquid densities change in regular and predictable fashion that may be reasonably approximated by the H<sub>2</sub>O–NaCl system (Driesner & Heinrich 2007) for natural vapour and brine compositions dominated by Na, K, and Fe chlorides. Consequently, the simple density trends shown in Figures 6 and 7 provide an efficient practical way for predicting vapour-liquid fractionation over the range of magmatic-hydrothermal conditions within an uncertainty less than one order of magnitude. Note that in S-poor water-salt systems, even at temperatures as high as 800 °C, Au and accompanying metals (Ag, Cu, Fe, not shown) enrich the liquid phase compared to the vapour.

Effect of sulphur on Au vapour-liquid partitioning. The experimental data in S-free or S-poor systems discussed above are in agreement with natural coexisting brine and vapour inclusions for all metals and metalloids, except gold and copper, which show systematic enrichment in the vapour phase (Fig. 5). The most plausible explanation of this enrichment is the formation of volatile species with sulphur, the second most important ligand after chloride (Heinrich et al. 1999). This hypothesis has recently been confirmed by experiments. The case of copper was discussed in detail in many recent papers (Pokrovski et al. 2008a; Frank et al. 2011; Simon & Ripley 2011; Kouzmanov & Pokrovski 2012; Lerchbaumer & Audétat 2012; Pokrovski et al. 2013b) and will be only briefly summarized here.

These experimental works showed that both at hydrothermal (300–500 °C) and magmatic (600– 800 °C) conditions, addition of reduced sulphur in the system does increase Cu partitioning into the vapour, compared to a S-free system, but with absolute  $K_{\text{vapour/liquid}}$  values never exceeding one, contrary to the natural data ( $K_{\text{vapour/liquid}}$  up to 100, Fig. 5). A plausible explanation of this systematic discrepancy was offered by recent measurements on natural and synthetic fluid inclusions in quartz reequilibrated with different fluid and melt compositions. These data revealed rapid diffusion of the Cu<sup>+</sup> ion through the quartz leading to large postentrapment changes in Cu concentrations in the inclusion (Li *et al.* 2009; Zajacz *et al.* 2009;

Lerchbaumer & Audétat 2012). Very recently, Seo & Heinrich (2013) analysed coeval vapour and brine inclusions trapped in coexisting topaz, garnet, and quartz from Mole Granite (Australia) and showed that, in contrast to all other metals and sulphur whose concentrations are identical in quartz- and topaz/garnet-hosted inclusions, Cu concentrations in vapour-like inclusions in quartz are 1-2 orders of magnitude higher than in coeval inclusions in topaz and garnet. Since the structure of these silicate minerals does not allow rapid diffusion of cations compared to quartz, these findings nicely confirm the experiments of Lerchbaumer & Audétat (2012). Seo & Heinrich (2013) developed a simple thermodynamic model according to which the diffusion occurs via the following exchange reaction between Cu<sup>+</sup> and H<sup>+</sup>, which have elevated diffusion coefficients in quartz but not in other silicate minerals:  $Cu_{external}^+ + H_{inclusion}^+ = Cu_{inclusion}^+ +$ H<sup>+</sup><sub>external</sub>. Its Gibbs free energy is the driving force of Cu<sup>+</sup> diffusion into quartz to compensate for the outward diffusion of H<sup>+</sup> from the inclusion-hosted acidic fluid. This reaction is favourable because of the large acidity acquired in the quartz-hosted S-rich inclusion during cooling through SO<sub>2</sub> disproportionation and precipitation of pyrite and chalcopyrite, whereas in the external fluid the acidity is rapidly neutralized by interaction with alkali aluminosilicate rocks (see below reactions 10 and 11 and corresponding discussions). The process continues until all reduced sulphur in the inclusion is consumed by precipitation with Cu<sup>+</sup> coming from outside according to the reaction above. This results in Cu/S ratios close to 2, similar to those in chalcopyrite in many natural vapour inclusions (Seo et al. 2009; Kouzmanov & Pokrovski 2012). Thus, the elevated copper contents in many vapour-like inclusions from porphyry deposits (Fig. 5) might be a post-entrapment modification, the extent of which depends on the thermal history of the host quartz and the chemical evolution of the external fluid. In constrast, Au and base metals like Zn, Fe, or Pb are likely not being strongly affected by such diffusion processes. Seo & Heinrich (2013) also suggest that Au<sup>+</sup> diffusion, if it does occur, is expected to be in opposite direction, that is, into the inclusion, so that Au concentrations analysed in high-T vapour-like inclusions from magmatic-hydrothermal deposits might probably be correct or at least represent minimal estimates. Other recent experiments in S-free systems also support these conclusions. Zajacz et al. (2009) imposed strong chemical gradients using concentrated HCl external solutions to test post-entrapment modifications of fluid and melt inclusions in quartz for a large number of elements including alkaline and alkaline earth elements, Cu and Ag, and found that only cations



**Fig. 8.** (a) Solubility of native gold as a function of temperature at 1000 bar pressure in model aqueous solutions of 10 wt% NaCl equivalent at pH 5 in equilibrium with the pyrite-magnetite-hematite (PMH), and pyrite-pyrrhotite-magnetite (PPM) oxygen and sulphur fugacity buffers, and at 0.1 wt% total dissolved sulphur and oxygen fugacity fixed by the magnetite-hematite buffer (MH). (b) H<sub>2</sub>S dissolved concentrations as a function of temperature in the three model systems above. (c) Au solubility as a function of pressure at 400 °C, 10 wt% NaCl, pH 5, in equilibrium with pyrite-magnetite-hematite ( $\sim$ 0.04 wt% S) and 0.1 wt%S with magnetite-hematite. (d) Au solubility as a function of salinity at 400 °C, 1000 bar, pH 5, in equilibrium with pyrite-magnetite-hematite. Calculations were performed using the HCh computer code (Shvarov 2008). Thermodynamic data for Au aqueous complexes are from this study (Table 5); those for minerals are from the SUPCRT database (Johnson *et al.* 1992), and those for sulphur species and other major fluid constituents and activity coefficients models are detailed in Pokrovski *et al.* (2009*a*, *b*). The dominant Au aqueous species are indicated. The grey area in panel (c) shows the domain of low-density vapour-like fluids (density < 0.3 g/cm<sup>3</sup>), for which calculations are not reliable at present.

with a charge of +1 and a radius equal to or smaller than 1.0 Å (Li<sup>+</sup>, Cu<sup>+</sup>, Na<sup>+</sup>, Ag<sup>+</sup>), diffused through quartz, whereas those having higher electric charges and/or larger radii (e.g. K, Rb, Cs) do not diffuse significantly, at least at the experimental duration (<10 days) and temperature (500–720 °C). Because Au<sup>+</sup> is similar in size to K<sup>+</sup> (~1.37 Å), it would not be expected to diffuse fast enough to create significant post-entrapment enrichment or depletion.

Direct measurements of gold vapour-liquid partitioning in model sulphur-rich salt-water systems are limited to two studies, to the best of our knowledge. Pokrovski *et al.* (2008*a*) reported  $K_{\text{vapour/liquid}}(\text{Au})$  values from 350 °C to 500 °C and  $P \leq 500$  bar in the Au–NaCl–KCl–NaOH system in the presence of up to 2 wt% of native sulphur or thioacetamide, using a hydrothermal reactor allowing accurate sampling of the vapour and liquid. Frank *et al.* (2011) measured vapour/brine and brine/melt partitioning of Au at 800 °C and 1000–1500 bar in the system NaCl–KCl–FeC<sub>2</sub>–H<sub>2</sub>O-haplogranite in the presence of (Cu,Fe)S or pyrrhotite. Figure 7 shows that with

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the addition of 1-2 wt% of S to the water-salt system at acidic-to-neutral pH and temperatures 350-500 °C, Au partition coefficients increase by up to 2 orders of magnitude, attaining values in favour of the vapour for Au ( $K_{Au} > 1$ ), whereas the partitioning of Zn, Fe, Pb (not shown) is almost unaffected. At magmatic conditions, the increase in Au volatility is weaker, by a factor of 2-3 on average, compared to S-poor compositions, but the scatter is large. Although the exact chemical identity and stoichiometry of Au complexes in the vapour phase remain unconstrained, it is very likely that gold forms uncharged complexes with reduced sulphur. The higher volatility of Au, compared to Cu and other base metals, is also consistent with the far greater stability of Au hydrogen sulphide v. chlorides species in aqueous solution and brine, as discussed above. Gold absolute concentrations measured in the vapour phase in equilibrium with metal both in hydrothermal and magmatic experiments attain several tens of ppm, which is comparable with Au contents measured in S-rich vapour-like fluid inclusions from porphyry Au-Cu deposits (Kouzmanov & Pokrovski 2012).

Another important factor controlling the vapour-liquid distribution of Au in S-rich systems is the fluid acidity. Because a neutral species in solution generally has a far greater volatility than its charged counterpart (Pokrovski et al. 2002a, 2008a), Au is expected to be more volatile in S-rich systems under acidic conditions where AuHS<sup>0</sup>, and probably AuHSH<sub>2</sub>S<sup>0</sup>, are more abundant in the liquid phase than  $Au(HS)^{2-}$  (see above). It can be seen in Figure 7 that, at similar H<sub>2</sub>S concentrations in the system (~0.5 wt% S), Au vapour-liquid partitioning coefficients in the case where the liquid phase pH is below 5 are systematically higher than those at the liquid-phase  $pH \ge 6$ , reflecting the change of the dominant Au species in the liquid (e.g. see Fig. 9a below). Vapour-liquid unmixing of a neutral-to-basic fluid in which  $Au(HS)_2^-$  is dominant will thus not be favourable for Au fractionation into the vapour phase.

### Gold speciation and solubility in magmatic fluids and fluid-melt partitioning

Hydrothermal Au-bearing fluids are often sourced from magmas (e.g. Hedenquist & Lowenstern 1994). This section briefly summarizes the existing data on Au contents, distribution, and partitioning in magmatic systems containing aqueous fluids, silicate melts, and sulphide melts/minerals, based on available high-precision micro-analytical data both from natural magmatic rocks and glasses and laboratory experiments. Natural systems. Table 6 summarizes the available data on gold concentrations measured in volcanic rocks, silicate glasses, fluids, and sulphide minerals. Most natural silicate melts contain gold at levels of <1-10 ppb, which is much lower than the ppm-level Au concentrations obtained in laboratory experiments in similar systems saturated with metallic gold (see below). The much lower natural Au concentrations mean that most natural magmatic systems are largely undersaturated with Au; this is consistent with the absence of sensu stricto magmatic gold deposits. By contrast, silicic melt and aqueous fluid inclusions from magmatic systems spatially related to Cu-Zn massive sulphide ore deposits (Vikent'ev et al. 2012) are highly enriched in gold, with tenors attaining several ppm, which approach the level of gold saturation in hydrous Cl-S-bearing silicic systems (Table 6). Similarly, measured gold contents both in fluid and sulphide melt inclusions in minerals from magmatic rocks hosting porphyry-type Au-Cu deposits attain levels of sub-ppm to ppm levels (Ulrich et al. 1999; Halter et al. 2002, 2005), approaching the experimental concentrations in the presence of metallic gold in hydrous S-bearing silicate melts (see below).

Gold concentrations in natural silicate glasses from evolved arc-related magmatic rocks in subduction zones display a dependence on SiO<sub>2</sub> content, by showing maximum values, up to  $\sim 10$  ppb, at  $\sim 60$  wt% SiO<sub>2</sub> or an mg# number of 40 (mg# = Mg/(Fe<sub>total</sub> + Mg) × 100 mol%) in a large range of rocks, from basalt to rhyolite (Moss et al. 2001; Sun et al. 2004; Jenner et al. 2010). In these arc-related magmas, the presence of magnetite crystallizing below 60 wt% SiO<sub>2</sub> marks the abrupt decrease of Au, Ag, and Cu contents to  $\sim 1$  ppb, which are close to those in MORB's and primitive mantle (Sun et al. 2004; Jenner et al. 2010). Fractional crystallization of granitic rocks hosting porphyry Cu-Au-Mo deposits was also found to lead to gold enrichment by a factor of 10-100 in residual silicate melts (up to 100 ppb, Mustard et al. 2006). The redox state  $(f_{O_2})$  and aluminum saturation index (ASI = AI/(Na + K + Ca)) in mol%) of the melt are also important factors affecting Au contents. For example, Connors et al. (1993) and Sisson (2003) reported elevated Au contents (5-35 ppb) in alkali mafic glasses and peralkaline felsic rocks (ASI < 1), with the highest Au concentration values (>30 ppb) being related to the most alkaline glasses containing native gold inclusions. Borisova et al. (2006) also reported high gold concentrations (up to 22 ppb) in hydrous adakitic glasses of rhyolite composition with ASI > 1 under oxidizing conditions  $(SO_2)$  $H_2S > 1$ ). More recently, Ishimaru *et al.* (2011) discovered in mantle wedge-derived xenoliths a new



**Fig. 9.** Solubility of native gold at 1000 bar and indicated temperatures in model 10 wt% NaCl equiv. aqueous fluids: (**a**) as a function of pH in equilibrium with the magnetite-hematite assemblage (MH) and 0.013 m H<sub>2</sub>S (~0.04 wt% S) in solution; (**b**) as a function of H<sub>2</sub>S dissolved concentration, pH 5, and oxygen fugacity fixed by magnetite-hematite (MH); (**c**) as a function of oxygen fugacity (log $f_{O_2}$ , in bars) at 0.1 wt% total dissolved sulphur, together with (**d**) corresponding distribution of sulphur species in the fluid. Vertical dashed lines in panels (c) and (d) indicate the oxygen fugacity of the major mineral buffers. QFM, quartz-fayalite-magnetite; NNO, nickel-nickel oxide; MH, magnetite-hematite.

type of S-rich silicate melt or silicate-bearing aqueous fluid concentrating Au, PGE, and other chalcophile metals (Cu, Ni). Their findings suggest that metasomatic reactions of such a fluid/melt with the mantle wedge resulted in Au, PGE, and volatile enrichment of the upper mantle (Ishimaru *et al.*, pers. comm.).

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*Experimental anhydrous systems.* Gold concentrations in dry basaltic melts vary from a few ppb to a few ppm and strongly depend on redox conditions (Table 6). Gold valence state in these melts has been established to be  $Au^{I}$  in the form of  $AuO_{0.5}$ -like species, based on the dependence of gold solubility on oxygen fugacity (Borisov & Palme 1996, 2000; Brenan *et al.* 2005). The

monovalent state of Au has also been confirmed by <sup>197</sup>Au Mossbauer spectroscopy in synthetic goldruby silicate glasses (Wagner *et al.* 2000). At a constant redox potential, Au solubility in haplobasaltic melts was shown to slightly increase with increasing temperature (Borisov & Palme 1996).

*Experimental hydrous systems.* Since 1994, the number of experimental studies on gold solubility in melts, aqueous fluids, and sulphides in hydrous Cl- and S-bearing systems is rapidly increasing. Most of these experiments were conducted at elevated pressures, approaching those of magma differentiation in the crust, and under buffered oxygen and sulphur fugacity using sulphide and oxide mineral assemblages (Table 6). These measurements

report Au solubilities in silicate melts generally comparable with those in anhydrous systems at similar T and  $f_{O_2}$  conditions.

In hydrous systems saturated with metallic gold, two main phases concentrate gold at levels from ppm to wt%: an aqueous S/Cl-bearing fluid and a Fe-Cu sulphide liquid. For example, Frank et al. (2002), Hanley et al. (2005), and Simon et al. (2005) demonstrated that Cl-bearing (NaCl-HCl) vapour and brine may dissolve up to  $\sim 6000$  ppm Au, depending on the HCl content in the system at temperatures from 800 °C to 1000 °C. Frank et al. (2002) suggested that gold speciation in silicate melts at elevated HCl concentrations is dominated by chloride complexes forming according to the reaction:  $AuO_{0.5}^{si-melt+}HCI^{fluid} = AuCl^{si-melt} + 0.5$ H2Osi-melt. Similar Au chloride species (AuCl and/ or AuCl · HCl) are likely to form in an aqueous fluid in equilibrium with this melt, yielding gold fluid/melt partitioning coefficients in favour of the aqueous fluid ( $K_{\text{fluid/Si-melt}}$  is between 8 and 840 at 800 °C and 1 kbar; Frank et al. 2002; Simon et al. 2005, 2007b) mainly because of the far greater HCl concentration in fluid compared to melt. Even higher  $K_{\text{fluid/Si-melt}}$  values for Au (1000–10 000) were reported by Hanley et al. (2005) for similar systems at higher pressures (1.5 kbar) and by Frank et al. (2011) for S-bearing systems. The exact gold speciation in the fluid and melt in these experiments remains, however, unconstrained.

Botcharnikov et al. (2010) inferred the formation of Au-Cl and Au-S complexes in Cl,S-bearing hydrous rhyodacite and andesite melts based on dependences of Au solubility v. Cl and S concentrations. More recently, Botcharnikov et al. (2011) proposed Au-S-O-like and Au-Fe-S-O-like species in their experimental hydrous andesitic and basaltic melts based on evidence of maximum gold solubility attained during decomposition/ dissolution of iron sulphides supplying high amounts of reduced sulphur to the melt. Similarly, Jégo & Pichavant (2012) reported a gold solubility increase in Fe-poor hydrous silicic melts at conditions of sulphide saturation (<NNO – 1) up to the sulphide-sulphate transition (NNO + 0.5 to NNO + 2.0). Based on thermodynamic modelling and solubility dependences, these authors suggested polymeric Au<sub>2</sub>FeS<sub>2</sub> species at redox conditions close to NNO - 1 in S-bearing hydrous silicic melts. However, in situ spectroscopic measurements of gold molecular environment are required to confirm this hypothesis. Zajacz et al. (2012) studied the solubility of Au in hydrous andesite melts in the presence of salt and sulphur and demonstated that it exhibits a redox dependence similar to that in aqueous solution (see Fig. 9c below) by reaching a maximum at redox close to the sulphidesulphate transition (around NNO + 0.5 at 1000  $^{\circ}$ C).

They interpreted their data by the AuCl species in Cl-bearing, S-free systems and by AuHS and mixed (K/Na)AuS complexes in S-bearing systems. However, the interpretation of Au solubility in such sulphur-rich systems may be complicated by metallic gold nugget formation during the temperature rise and poorly known sulphur speciation, which may consist of species other than sulphide and sulphate, such as  $S_3^-$  and  $SO_2$  (Zajacz et al. 2012). Interestingly, similar alkali metal Au hydrogen sulphide complexes of the type  $(H_2S)_vAu(SH)(NaCl,KCl)_x$  were hypothesized by Zajacz et al. (2010) to explain the enhanced Au solubility in aqueous S- and NaCl/KCl-bearing fluid phases at similar conditions (1000 °C, 1.5 kbar, NNO – 0.6,  $S_{tot}$  up to ~10 wt%, NaCl or KCl  $\leq 0.7$  m, Au  $\sim$  several 100s ppm). In addition to the effect of alkalis, their study also showed that hydrogen sulphide complexes dominate over chlorides even at 1000 °C at S and Cl concentrations typical of high-temperature vapours. Revealing the exact nature and structure of such new Au-carrying species requires in situ spectroscopic approaches both for Au and S.

The majority of experiments clearly show that Au is strongly concentrated in Fe/Cu sulphide liquids compared to silicate melts. For example, Bezmen et al. (1994) obtained Fe sulphide phases enriched in gold up to  $\sim$ 3 wt%, with Au partitioning coefficients  $K_{\text{sulphide/Si-melt}}$  reaching  $10^3 - 10^4$ . Similarly, Jugo et al. (1999), Bell et al. (2009), and Frank et al. (2011) reported in Cl-S-bearing granite systems Au enrichments in sulphides from  $\sim 0.7$  to 6 wt% Au (depending on the sulphide), with corresponding K<sub>sulphide/Si-melt</sub> values of 1000-10 000. Li & Audétat (2012) reported sulphide melt-mafic silicate melt partition coefficients for Au of the order of  $n \times 10^2 - n \times 10^3$  for much higher pressures (15-30 kbar), corresponding to upper mantle conditions. Simon & Ripley (2011) established an empirical dependence of the pyrrhotite-silicic melt partition coefficients on  $f_{S_2}$  for chalcophile metals (Au, Cu, Ag). Jégo & Pichavant (2012) also point to an important role of FeS in controlling gold solubility in S-bearing hydrous melts. Very recently, Zajacz et al. (2013) conducted systematic measurements of Au, Cu, and Ag solubility and partitioning in reduced sulphur magmas of basalt to rhyolite compositions and demonstrated that pyrrhotite/silicate melt partitioning coefficients for Au ( $K_{sulphide/Si-melt}$ ) increase by a factor of  $\sim 5$ from basalt ( $K \sim 200$ ) to rhyolite ( $K \sim 1100$ ), which is primarily controlled by the FeO and FeS activities in the silicate melt. Copper behaves similarly to gold with comparable partition coefficients, whereas Ag exhibits much lower K values ( $\sim$ 50) independent of melt composition. These authors concluded that the Au (and Cu) budget is largely

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Location / Method	System	T °C, P kbar, $f_{O_2}, f_{S_2}$	Au in fluid, ppm {speciation}
Natural magma World	<i>tic-volcanic systems</i> Fresh silicic volcanic rocks and glasses	-	-
Papua New	Fresh volcanic glass and glassy	_	_
Guinea Argentina	rocks Magmatic rocks hosting porphyry Au–Cu deposit Bajo	$1000^{\circ}, \\ \ge 3.5 \text{ kbar},$	~2.0
Hawaii	de la Alumbrera Anhydrous basalt, hawaiite,	$\sim 6 \text{ wt}\% \text{ H}_2\text{O}$ QFM	-
Papua New Guinea	Basalt to rhyodacite glasses	-0.3 + 1.3 QFM+2	_
Philippines	Rhyolite/dacite melts (adakites) and aqueous fluid inclusions	$760-900^{\circ}$ 2–10 kbar	-
Eastern Manus basin	Arc-related basalt to rhyolite, and MORB from Atlantic and Pacific ocean	-	-
Ural	Rhyodacite melt and aqueous fluid inclusions with 1–6 wt% NaCl eq.	700-850° 5-9 kbar	~8
<i>Experimental a</i> CAF	nhydrous systems saturated with met Basalt and sulphides	tallic Au $1200 ^{\circ}\text{C}, 1 \text{ bar}$ $\log f_{\circ} = -9.2$	_
CAF	Haplobasalt	$1300-1480^{\circ}$ , 1 bar, $\log f_{O_2}$ from -11.5 to -0.7	-
CAF	Basalt & Fe-Ni liquid	1250°,	-
CAF	Fe-free haplobasalt	1200–1500°, 1 bar, QFM–2 to QFM+2	-
CAF	Basalt – olivine	1260–1350°, 1 bar QFM+0.6 to QFM+5.4	-
Experimental h PCA	ydrous systems saturated with metall MSS + Cu-rich sulphide liquid + $H_2O \pm CO_2 - CH_4 -$ $H_2 = 0 \pm CO_2 - CH_4 -$	<i>lic gold</i> 900°, 10 kbar	150-270
HPGA	H <sub>2</sub> S-NaCl hund Mafic to intermediate melt & sulphides + NaCl + water	1200-1300°; 100-	_
CSPV	Haplogranite + pyrrhotite (po) + iss + water	$\begin{array}{l} 850^{\circ}, 1 \text{ kbar} \\ \log f_{\mathrm{O}_2} = -13.2 \pm 0.3, \\ \log f_{\mathrm{S}_2} = -1 \pm 0.7 \end{array}$	-
CSPV	Haplogranite + 70 wt% NaCl eq. aqueous brine with variable HCl	$800^{\circ}$ , 1 kbar, NNO [HC1] <sup>brine</sup> = 3000-40 000 ppm	40–840 {AuOH - at low HCl}
CSPV	Granite melt and 20–70 wt%	600–800 °C, 1.5 kbar, NNO,	$\{AuCl_2 \Pi at \Pi g\Pi HCl\}$ 900–6000 $\{AuCl_AuCl_H\}$
CSPV	Haplogranite, aqueous hald Vapour ± brine	$800 \degree C, 1.1 - 1.45 \text{ kbar, NNO}$ [HCl] <sup>vapour</sup> = 670 - 1100 ppm	$\begin{cases} AuCl, AuCl2H \\ 5-36 (vapour) \\ \{AuOH^{vapour}\} \\ 28-50 (brine) \\ \{AuCl2H\} \end{cases}$

**Table 6.** Major published data on natural gold contents and experimental gold solubility and partitioningin silicate and sulphide melts and aqueous fluids

# GOLD SPECIATION IN GEOLOGICAL FLUIDS

Au in melt or glass, ppm {speciation}	K <sub>fluid/melt</sub>	Au in sulphide, ppm	$K_{ m sulphide/Si-melt}$	References
0.0006-0.005 (peralkaline) $\leq 0.0001-0.0005$ (peraluminous) $\sim 0.0005$	-	_	-	Connors et al. (1993)
(intermediate) 0.001-0.015 (maximum at a .57 wt% SiQ )	_	-	-	Moss et al. (2001)
at $\sim 37$ wt% SIO <sub>2</sub> ) bdl	-	<0.1-4.3 (FeS melt)	-	Halter <i>et al.</i> (2002, 2005)
0.001-0.035	_	-	-	Sisson (2003)
0.0009-0.008		-	-	Sun et al. (2004)
0.00064-0.022	_	-	_	Borisova et al. (2006)
$\sim$ 0.001 (Mg# <40, SiO <sub>2</sub> <60 wt%, magnetite), up to 0.007 (Mg# > 40,	-	-	-	Jenner et al. (2010)
no magnetite) $\sim 1.3$ (melt inclusions)	~6	-	_	Vikent'ev <i>et al.</i> (2012)
0.0004-0.0013	-	0.6-0.9	$1200\pm900$	Stone et al. (1990)
$0.3-52$ (depending on $f_{O_2}$ )	-	-	_	Borisov & Palme (1996)
{AuO <sub>0.5</sub> } 0.0007–0.013	_	0.8-172	$1210\pm950$	Crocket et al. (1997)
0.04-0.8 (QFM-2) 0.1-2.5 (QFM) 0.4-8.0 (QFM+2)	_	-	-	Borisov & Palme (2000)
{Au <sup>+</sup> } 0.9–12.3	_	-	_	Brenan et al. (2005)
-	-	-	-	Ballhaus et al. (1994)
0.043-12	_	70-31 000	$16000\pm4000$	Bezmen et al. (1994)
2.1–9.3	-	16 000–24 000 (iss) 340–640 (po)	$5700 \pm 2200$ (iss/Si-melt) $140 \pm 40$ (po/Si-melt)	Jugo et al. (1999)
$\sim 1$ {Au <sup>0</sup> - at low HCl},	40-840 (at HCl <10 000 ppm)	-	(po/ bi men) _	Frank et al. (2002)
{AuCI at high HCI} $0.2-1.2$	2600-12 000	-	_	Hanley et al. (2005)
0.25-0.50	8-72 (vapour/melt)	-	_	Simon <i>et al.</i> (2005)
	56-100 (brine/melt)			

(Continued)

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#### Table 6. Continued

Location / Method	System	T °C, P kbar, $f_{O_2}, f_{S_2}$	Au in fluid, ppm {speciation}
CSPV	Haplogranite, brine, vapour	800°, 1–1.45 kbar	4–41 (vapour)
CSPV	Haplogranite and aqueous fluid	$800^{\circ}$ , 1.2 kbar; NNO	27-53 (brine) ~30 (fluid, S-free) ~12 (fluid, S-bearing)
CSPV	Haplogranite, sulphides (mss + iss + sulphide liquid), magnetite, NaCl-KCl-H <sub>2</sub> O fluid	$800^\circ$ , 1.5 kbar; NNO, $\log f_{S_2} = -5 \div 0$	-
IHPV	Cl-S-bearing hydrous system:	$1050^{\circ}$ , 2 kbar; NNO	_
RQ-TZMV	Quartz and NaCl/KCl/LiCl/ CaCl <sub>2</sub> -HCl-S-H <sub>2</sub> O fluid	1000°, 1.5 kbar; NNO-0.6 to NNO+1.9	1.9–4.3 (Na/KCl-free; up to 682 (Na/ KCl-bearing) AuCl, Na/KAuCl <sub>2</sub> , Na/ KAu(HS)
IHPV	Basalt, andesite, FeS, CaSO <sub>4</sub> , H <sub>2</sub> O	1050°, 2 kbar; QFM-0.4 to QFM+3.3	-
CSPV	Haplogranite, brine, vapour $\pm$ sulphides	$800^{\circ}$ , 1 kbar; NNO	17–240 (brine), 6–28 (vapour)
IHPV	S-bearing hydrous (undersaturated) dacite	$1000^\circ$ , 4 kbar $a_{\mathrm{H_2O}} \leq 1$ $\log f_{S_2} = -4 \text{ to } +3$	vapour phase not analysed
RQ-TZMV	$\begin{array}{c} \text{Andesite} + \text{H}_2\text{O} + \text{ K/NaCl}, \\ \text{FeCl}_2, \text{ S} \end{array}$	1000°, 2 kbar NNO-0.5 to NNO+1.8	-
PCA	Mafic silicate melt (SM) + monosulphide solid solution (MSS) + sulphide liquid (SL)	1175–1300°, 15–30 kbar QFM–3.1 to QFM+1.0	-
RQ-MHC	Basalt, dacite, andesite, rhyolite, H <sub>2</sub> SO <sub>4</sub> aqueous solution (5-9  wt%S), AuCuAg alloys	900–1030° 2 kbar NNO–0.8 $\log f_{S_2} \sim -3$ to $-2$	-

IHPV, internally heated pressure vessel; CSPV, cold-seal pressure vessel; CAF, controlled atmosphere furnace; PCA, piston cylinder apparatus; HPGA, high pressure gas apparatus; RQ-TZMV, rapid quench titanium-zirconium-molybdenum vessel; RQ-MHC, rapid quench molybdenum-hafnium-carbide pressure vessel;  $T-P_{f_{S_2}}$ , temperature-pressure-oxygen-sulphur fugacity;  $a_{H_2O}$ , water activity; K, partitioning coefficient; Si-melt, silicate melt; iss, intermediate solid solution; mss, monosulphide solid solution;

controlled by pyrrhotite in intermediate-to-felsic magmas.

In summary, the main messages from these results are the following: (1) Gold is concentrated in magmatic aqueous Cl- and S-bearing fluids and iron-copper sulphides at levels of  $100-10\ 000$  ppm. (2) Gold solubility both in hydrous and anhydrous silicate melts is several orders of magnitude lower (0.*n* to *n* ppm); it is generally

proportional to  $f_{O_2}$ ,  $f_{S_2}$ , and  $m_{Cl}$ , suggesting the formation of Au<sup>1</sup> oxygen, sulphide, or chloride species. (3) Au solubility in silicate melts reaches a maximum at the sulphide-sulphate redox transition, similar to that in aqueous fluids. (4) The presence of iron sulphide is likely to be the most important controlling factor of Au behaviour in natural silicate melts and the source of this element in degassing volatile aqueous phases.

#### GOLD SPECIATION IN GEOLOGICAL FLUIDS

Au in melt or glass, ppm {speciation}	$K_{\mathrm{fluid/melt}}$	Au in sulphide, ppm	$K_{ m sulphide/Si-melt}$	References
0.5 - 0.9 (ASI = $0.83 - 1.0$ )	N.A.	-	_	Simon <i>et al.</i> (2007 <i>a</i> )
2.7 (ASI = $1.02-1.13$ , S-free) $\sim 0.6$ (S-bearing)	$15 \pm 2.5 \text{ (vapour/melt, S-free),} \\ 12 \pm 0.3 \\ \text{(vapour/melt, S-bearing)}$	-	_	Simon <i>et al.</i> (2007 <i>b</i> )
0.02-0.65	_	9-286 (mss); 107-7220 (iss); 200-64 000 (Fe-Ni-Cu-S)	2300-10 000 (mss/si-melt)	Bell et al. (2009)
0.2-2.5 {Au-Cl <sup>si-melt</sup> , Au-S <sup>si-melt</sup> }	_	_	_	Botcharnikov <i>et al.</i> (2010)
_	-	-	_	Zajacz <i>et al.</i> (2010)
up to 8 {Au-S- $O^{\text{si-melt}}$ , Au-Fe- S- $O^{\text{si-melt}}$ }	-	200-1400	100–300 (sulphide/ Simult)	Botcharnikov <i>et al.</i> (2011)
0.1-0.4	~1300 (brine/ Si-melt), 120 (vapour/ Si-melt)	300-500	1100–5000 (iss/Si-melt)	Frank et al. (2011)
$\begin{array}{c} 0.25-5\\ {Au}^{\text{Osi-melt}}, AuO_{0.5}^{\text{Si-melt}} \\ \text{NNO+1.5};\\ {Au} \text{ FeS}^{\text{Si-melt}} \text{ of } \text{NNO} = 1 \end{array}$		_	_	Jégo & Pichavant (2012)
Up to 5, increase with increasing S and Cl; max Au solubility is at NNO+0.5; {AuCl, AuHS, Na/KAuS}				Zajacz et al. (2012)
			$3400 \pm 1200$ (MSS/SM) $180 \pm 80$ (SL/SM)	Li & Audétat (2012)
0.02-4.3 {AuSNa <sup>si-melt</sup> }	_	20-600	$\frac{180 \pm 20 \text{ (basalt)}}{900 \pm 210}$ (dacite) 1150 \pm 50 (rhyolite)	Zajacz et al. (2013)

(Fe-Ni) or Fe-Ni-Cu liquid, sulphide liquid; po, pyrrhotite; IQF, iron-silica phase-fayalite oxygen buffer; QFM, quartz-fayalite-magnetite oxygen buffer; NNO, nickel-nickel oxide oxygen buffer; ASI, aluminium saturation index; NaCl eq., salt content of the fluid expressed in wt% of NaCl equivalent; ' $\sim$ ' means approximate value; '-' means not applicable or not analysed; bdl, below detection limit.

Factors of gold preconcentration and mobilization in melts. These features of Au behaviour determine the sources of Au for hydrothermal deposits and the ore-forming potential of magmas. Simon & Ripley (2011) discussed several mechanisms which may increase ore-forming potential of a given magmatic system due to sulphide dissolution. Among them are the following: solidification/degassing from the early cumulus assemblage during magma crystallization (Boudreau & Meurer 1999); degassing from magma saturated with an aqueous fluid; interaction with a hydrothermal fluid phase (e.g. Stavast *et al.* 2006); and magma oxidation (Bell & Simon 2011). An important mechanism leading to concentration of Au, Cu, and Ag in magmatic Fe– Cu sulphide minerals is reduction of sulphate to sulphide and oxidation of ferrous iron to ferric iron upon fractional crystallization of a Fe<sup>II</sup>-bearing

mafic silicate melt, leading to crystallization of magnetite and triggering the saturation in Cu-rich sulphide phase. This sulphide phase (presumably of bornite-like composition) efficiently scavenges Au and Ag from the silicate melt in arc-related magmas (e.g. Jenner et al. 2010). The high contents of chalcophile elements such as gold, copper, and silver in magmatic iron sulphides make them an important source of these metals for the degassing aqueous fluid at depth (e.g. Larocque et al. 2000). Crustal assimilation is also an important phenomenon leading to magma saturation in volatiles and contributing to ore-forming potential (Russell et al. 1995; Borisova et al. 2012a, 2013a). Mixing or hybridization of a sulphide-bearing basaltic magma with an hydrous sulphide-undersaturated andesitic or dacitic magma may also be an important mechanism for supplying chalcophile metals to aqueous S-bearing fluid due to dissolution of the basalt-hosted sulphides (e.g. Hattori & Keith 2001; Halter et al. 2005; Borisova et al. 2012b). Gold-to-copper ratios in sulphide melt inclusions from magmatic rocks hosting porphyry deposits are identical to those in the magmatic fluid and bulk ore, implying a magmatic sulphide source for both Au and Cu (e.g. Ulrich et al. 1999; Halter et al. 2002). Based on experimental data in hydrous S-bearing systems, Botcharnikov et al. (2011) suggested that gold-rich basaltic-to-andesitic magmas can be generated in sulphide-saturated mantle at relatively oxidizing conditions corresponding to the sulphide-sulphate boundary, which may occur above subduction zones and mantle plumes. These authors propose the two main controls on the genesis of Au-enriched arc magmas: (1) metasomatism of the mantle wedge by Au-enriched slabderived fluids; and (2) redox state and abundance of sulphur in the magmatic source.

# Major parameters controlling Au transport and precipitation in hydrothermal fluids

At the current state of our knowledge, quantitative modelling of Au transport as a function of different parameters of crustal fluids such as temperature, pressure, salinity, acidity, and redox conditions are only possible for the aqueous liquid and dense supercritical fluid phase (density >0.3-0.4 g/cm<sup>3</sup>), for which large amounts of experimental data and robust thermodynamic models (e.g. HKF) are available (see section "Gold chloride, hydrogen sulphide, and hydroxide species in aqueous solution and dense supercritical fluid"). This information allows quantitative evaluation of the effect of these parameters on Au speciation and solubility, assuming that the dominant aqueous gold species in the

majority of such fluids are those with the hydroxide, chloride, and hydrogen sulphide ligands (see section "Gold chloride, hydrogen sulphide, and hydroxide species in aqueous solution and dense supercritical fluid"). The effect of other sulphur ligands (section "The role of other sulphur-bearing forms for hydrothermal transport of gold") that may potentially be important in S-rich systems cannot be evaluated at present owing to the extreme scarcity of the data and insufficient knowledge of sulphur aqueous speciation itself. Keeping these limitations in mind, the dominant reactions controlling Au solubility in a typical aqueous hydrothermal liquid, vapour, and supercritical fluid containing salts and sulphur in the form of sulphate and sulphide below  $\sim 600$  °C and  $\sim 5$  kbar are assumed to be the following:

$$Au(s) + 2H_2S = Au(HS)_2^- + 0.5H_2 + H^+,$$
  
in near-neutral and alkaline fluids (10a)

$$Au(s) + H_2S = AuHS^0 + 0.5H_2$$
, in acidic fluids  
(10b)

$$Au(s) + H^+ + 2Cl^- = AuCl_2^- + 0.5H_2$$
, above  
450-500 °C in acidic saline fluids  
and brines (10c)

$$\begin{split} Au(s)+2H_2S &= Au(HS)H_2S^0+0.5H_2, \mbox{ tentative},\\ &\mbox{ in acidic S-rich fluids and vapours} \end{split}$$

$$Au(s) + H_2O = AuOH^0 + 0.5H_2,$$
  
in Cl-poor and S-poor fluids (10e)

$$Au(s) + H^{+} + Cl^{-} = AuCl^{0} + 0.5H_{2},$$
  
above 450-500 °C in acidic S-poor  
vapours. (10f)

The Au(HS) $H_2S^0$  species (reaction 10d) suggested for S-rich (>1 wt% S) acidic conditions remains tentative because of other possible alternatives (polysulphide, sulphite) and the limited T-Pdomain of its reported stability constants (Pokrovski et al. 2009b). Consequently, this complex was not considered systematically in the thermodynamic modelling below. Note, however, that its contribution to Au solubility is relatively low at S contents below 1 wt%, and its dependence on the major parameters is very similar to that of AuHS<sup>0</sup>; as a result, neglecting Au(HS)H<sub>2</sub>S<sup>0</sup> in solubility calculations below does not significantly affect the main trends. Gold hydroxide species (reaction 10e) appear to be minor compared to chlorides and sulphides in most Au ore-deposit contexts at naturally pertinent Cl and S concentrations. However, at

some high-temperature magmatic sulphur-poor fluid compositions, this or mixed hydroxide-chloride complexes might become more important (e.g. Simon et al. 2005), owing to the general increase of the stability of ionic-like complexes with harder ligands (OH<sup>-</sup> and Cl<sup>-</sup> v. HS<sup>-</sup>) with increasing temperature and decreasing the fluid dielectric constant (Brimhall & Crerar 1987). Gold monochloride (reaction 10f) is minor in fluids above 0.1 wt% salt at hydrothermal temperatures ( $< \sim 500$  °C), but it may contribute at magmatic temperatures and in the vapour phase in S-poor systems for the same reasons as those for AuOH above. Thus, reactions 10a, b, and c are expected to adequately reflect the major hydrothermal controls on gold behaviour, at least in fluids containing less than 0.5-1.0 wt% S.

Figure 8 shows the solubility of native gold and the range of predominance of its main species as a function of the three key parameters-temperature, pressure, and salinity-at buffered or fixed sulphur concentrations typical of the majority of Au ore-forming environments. Figure 9 displays calculated Au solubility as a function of acidity, sulphur content, and redox potential within the typical range of these parameters in the crust. Below, we discuss the effect of each of these parameters on Au solubility. In addition, the effect of two ubiquitous components often associated with hydrothermal gold deposits, carbon dioxide and arsenic, will be evaluated from a physical-chemical point of view. Finally, possibilities of Au colloidal and hydrocarbon transport will be tackled. Solubility controls on other metals usually accompanying gold such as Cu, Ag, and Mo have recently been discussed elsewhere (Kouzmanov & Pokrovski 2012; Pokrovski et al. 2013a) and thus will be only briefly mentioned here for the sake of completeness (where necessary).

Temperature. Gold solubility in aqueous fluids circulating in environments where sulphur and oxygen fugacity are buffered by common iron oxide and sulphide mineral assemblages (PPM = pyrite-pyrrhotite-magnetite, and PMH = pyritemagnetite-hematite) shows a pronounced increase with increasing temperature, from < 0.001 ppm Au below 200 °C to  $\sim 10$  ppm Au above 500 °C. This increase is accompanied by progressive changes of the dominant Au species in the fluid from AuHS<sup>0</sup>( $\pm$ AuOH<sup>0</sup>) below 200 °C, to AuHS<sup>0</sup> + Au(HS)<sub>2</sub><sup>-</sup> between 250 °C and 450 °C, and to AuCl<sub>2</sub><sup>-</sup> above 500 °C (Fig. 8a). These changes in Au solubility and speciation with temperature reflect (1) the increase of H<sub>2</sub>S content in the fluid in equilibrium with the Fe-bearing sulphide minerals (from  $\sim 10^{-5}$  at 150 °C to 0.5 mol/kg at 500 °C, Fig. 8b), and (2) the increasing tendency at elevated temperatures for stabilizing ionic-bond complexes with harder ligands, such as chloride compared to sulphide (e.g. Brimhall & Crerar 1987). The large increase in solubility with temperature in these systems is also typical for base metal (Cu, Fe, Zn, Pb) sulphide minerals but not for the same reason as for Au. These metals form, over the whole T range, almost exclusively chloride complexes whose stability largely increases with increasing temperature (Barnes 1997; Kouzmanov & Pokrovski 2012).

Gold solubility in Fe-poor fluids (i.e. in the absence of pyrite) at a constant sulphur concentration (0.1 wt% S, which is typical of hydrothermal fluids) exhibits a particular temperature trend (Fig. 8a), not observed for any base metal. From 150 to 350 °C, it shows elevated dissolved Au concentrations of  $\sim 1-10$  ppm, with a weakly pronounced maximum at 200-250 °C. This is in agreement with the temperature evolution of  $Au(HS)_2^-$  stability constants (Fig. 2), which show a maximum at these temperatures. Above 250 °C, Au dissolved concentrations decrease, show a weak minimum around 400 °C, and then increase again above 450 °C due to the growing stability of AuCl<sub>2</sub>. Thus, oxidized magmatic fluids of moderate salinity, for example, those typical for porphyry systems (Sillitoe 2010; Richards 2011), are able to transport significant amounts of Au above 450 °C as chloride species, whereas Au transport in epithermal environments (<350 °C) is strongly conditioned by the amount of ferrous iron in the fluid and rock, which is the main sink for hydrogen sulphide in the form of pyrite (see below).

*Pressure*. A typical pressure effect on Au solubility is shown in Figure 8c. Similar to other ore minerals, the pressure influence appears to be quite weak compared to that of temperature for liquid and supercritical fluids at densities above  $\sim 0.5 \text{ g/cm}^3$ . This is explained by the low compressibility of dense water and a weak effect of pressure on the solvent dielectric constant and density, which control the thermodynamic properties of aqueous species (Mesmer *et al.* 1988; Shock & Helgeson 1988). The minor increase of Au solubility with decreasing pressure apparent in Figure 8c is mostly due to the increase in dissolved H<sub>2</sub>S concentration in the fluid (not shown) in the system in equilibrium with Fe sulphides.

At pressures corresponding to the vapour-like domain (shown by grey color in Fig. 8c), the available experimental data and models do not allow reliable predictions of Au solubility. The preferential partitioning of Au into vapour v. saline liquid revealed by rare existing experiments (e.g. Pokrovski *et al.* 2008*a*) and analyses of natural fluid inclusions (Kouzmanov & Pokrovski 2012; references therein) suggest that uncharged hydrogen

sulphide or chloride complexes might be stabilized in the vapour phase with decreasing pressure (see section "Vapour transport and vapour-liquid partitioning of gold"), but their stoichiometry and ligation number may be different from those of the negatively charged Au bis-hydrogen sulphide and dichloride complexes dominant in dense aqueous fluid. However, even within our limited knowledge of the low pressure domain, the effect of pressure itself in a single-phase fluid for the majority of geological situations in the crust is likely to be of secondary importance compared to that of temperature, sulphur amount, and redox potential. An indirect pressure effect, generating vapour-liquid separation or boiling, will be discussed in section "Fluid-phase controls on gold ore formation in hydrothermal systems."

Salinity. At temperatures below 500 °C and nearneutral pH, the presence of salts (i.e. chloride) does not significantly influence Au solubility (Fig. 8d). The small effect of chloride is consistent with the weak stability of AuCl<sub>2</sub><sup>-</sup> at such moderate temperatures and the predominance of hydrogen sulphide complexes, which are the solubility-controlling species. This Au speciation feature contrasts with the pronounced solubility increase with salinity for sulphide ore minerals of most base metals (Cu, Fe, Zn), which form chloride complexes in hydrothermal fluids (Hemley & Hunt 1992; Hemley et al. 1992; Yardley 2005; Kouzmanov & Pokrovski 2012; references therein). The salinity effect on gold may be more pronounced at acidic and S-poor conditions (pH < 4), but it is likely to be attenuated by the general decrease of salinity in a cooling magmatic fluid subjected to boiling and mixing with meteoric waters. In contrast, in magmatic brines above 500 °C, chloride complexes are expected to play a major role in gold transport, provided that Au species with other sulphur-bearing ligands (e.g.  $SO_2$  and  $S_3^-$ ) turn out to be insignificant at such conditions (see section "The role of other sulphurbearing forms for hydrothermal transport of gold").

Acidity. The fluid pH (by definition, pH is the negative decimal logarithm of the activity of free protons in solution,  $pH = -log_{10}a_{H_{+}}$ ) directly affects the concentrations of the charged complexes  $AuCl_{2}^{-}$  and  $Au(HS)_{2}^{-}$  in equilibrium with native metal because their formation reactions involve protons. The fundamental difference between these two species is that the former consumes H<sup>+</sup> (reaction 10c) and the latter produces H<sup>+</sup> (reaction 10a). Uncharged complexes (e.g. AuHS, Au(HS) H<sub>2</sub>S) are not affected by pH changes because no H<sup>+</sup> is involved in their formation (e.g. reactions 10b, d). It follows from reactions 10, a–f that, in a typical CI- and S-bearing fluid, Au solubility increases at both acidic and basic pH and passes through a minimum at near-neutral pH (Fig. 9a). With decreasing temperature and salt content, this minimum shifts towards a more acidic pH. Again, the effect of pH is quite different for the major metals (Fe, Cu, Zn) whose sulphide mineral solubilities decrease dramatically with increasing pH over the whole naturally relevant range (pH  $\sim$ 3– 9). For example, with all other parameters being equal, a pH change from 4 to 5 yields a 100-fold decrease in pyrite and sphalerite solubility at 400 °C and 10 wt% NaCl (Kouzmanov & Pokrovski 2012, not shown), whereas Au solubility is almost unaffected (Fig. 9a).

Thus, at epithermal conditions (<300 °C), fluid buffering by alkali and alkali-earth aluminosilicate rocks or carbonates, yielding a fluid pH between 5 and 7, may be favourable for Au transport as  $Au(HS)_2^-$ , whereas at porphyry-deposit temperatures (>400 °C), neutralization of the acidic fluid by interaction with such rocks will induce AuCl<sub>2</sub> breakdown and gold precipitation. However, it should be kept in mind that, in natural contexts, changes in fluid pH are often accompanied by changes in both sulphur speciation itself and solubilities of major metal sulphides, so that the final effect of fluid-rock interactions on the fluid capacity to transport gold will depend on a given natural case (see section "Fluid-phase controls on gold ore formation in hydrothermal systems" below).

Reduced sulphur. The effect of H<sub>2</sub>S is straightforward for all Au hydrogen sulphide complexes, by favouring their stability and thus gold solubility (reactions 10a, b, and d). It can be seen in Figure 9b that, at near-neutral pH buffered by silicate rocks, fluids with H<sub>2</sub>S contents above 1000 ppm S ( $\approx 0.03 \text{ mol/kg}$ ) are capable of transporting, over a wide temperature range, ppm-level Au concentrations (which is  $\sim 1000$  times higher than Au average tenors in the Earth's crust). At sulphur contents of several wt%, occurring in fluids from magmatic porphyry deposits and hightemperature metamorphic settings (Seo et al. 2009, 2012; Tomkins 2010), Au(HS) $_{2}^{-}$  and, potentially, other sulphide and/or polysulphide complexes may transport 100s to 1000s ppm of Au without reaching saturation with the metal. The effect of reduced sulphur is fundamentally different for base metals that are transported as chloride complexes but precipitate as sulphide minerals. Thus, high H<sub>2</sub>S concentrations are not favourable for Zn, Fe, Ag, and Mo mobility but are likely to be a major condition for efficient Au transport.

One of the major controlling factors of Au behaviour in geological fluids is, thus, the availability of reduced sulphur, which is often determined by the capacity of an Fe-bearing rock and/or dissolved ferrous iron to scavenge  $H_2S$  from the fluid. A second major parameter is the speciation of sulphur itself in the fluid phase, which is highly sensitive to redox conditions, as will be shown below. A third issue, which cannot be quantified at present, is the potential existence of other  $H_2S/HS^-$ -bearing species of different stoichiometries and/or of Au complexes with polysulphide ( $\pm$  sulphite) ligands in S-rich fluids (see section "The role of other sulphur-bearing forms for hydrothermal transport of gold" above).

Redox potential. The effect of redox conditions (which are usually quantified in terms of oxygen fugacity,  $f_{O_2}$ , and assuming the equilibrium between O<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O in the fluid at elevated temperature:  $H_2 + 0.5O_2 = H_2O$ ) on Au solubility is double, as shown in Figure 9c, d. First, in the domain of predominance of H<sub>2</sub>S under reducing conditions, native Au solubility is proportional to  $f_{O_2}$ , as can be seen in Figure 9c (or inversely proportional to  $f_{\rm H_2}$ , as shown by reactions 10a-f). At temperatures below 500 °C, this trend holds up to relatively high oxygen fugacities, corresponding to the magnetite-hematite buffer (MH). At more oxidizing conditions, however, a second effect takes place, which is the oxidation of H<sub>2</sub>S to sulphate or sulphur dioxide (depending on pH). This reinverses the Au solubility trend v.  $f_{O_2}$  because of the decreasing concentration of  $H_2S$  in favour of the more oxidized S species, which are not known to bind Au. At highly oxidizing conditions (above MH), where sulphate largely dominates, gold solubility in salt-bearing fluids generally increases again owing to the formation of chloride species. Although such oxidizing conditions are rare in natural high-temperature settings, they may probably occur in some iron oxide Cu-Au (IOCG) deposits (e.g. de Haller & Fontboté 2009). It follows from the trends of Figure 9c, d that the maximum capacity for Au transport occurs at redox conditions slightly below those of MH, when the fluid H<sub>2</sub>S fraction is still high enough. Such conditions are typical for porphyry Cu-Au deposits (next two sections).

Interestingly, the effect of redox is very similar for Au solubility in S- and Cl-bearing hydrous silicate melts in which Au concentrations in equilibrium with the metal reach maximum values at the  $H_2S-SO_4$  transition and then decrease to more oxidizing conditions (Botcharnikov *et al.* 2011; Zajacz *et al.* 2012; see also section "Gold speciation and solubility in magmatic fluids and fluid-melt partitioning" above).

 $SO_2$  breakdown. Another factor complicating Au behaviour in the fluid phase, particularly in porphyry systems, is  $SO_2$  breakdown on cooling. This

is one of the major phenomena that might lead to Au fractionation from Cu and other base metals during the porphyry-to-epithermal transition. Cooling of  $SO_2$ -bearing magmatic fluid is accompanied by large changes in sulphur speciation itself, which, in turn, affect both H<sub>2</sub>S concentration and acidity, according to the reaction of  $SO_2$  disproportionation:

$$4SO_2 + 4H_2O = H_2S + 3HSO_4^- + 3H^+ \quad (11)$$

While this reaction does not cause significant redox changes because it is independent of oxygen fugacity, it is pH-dependent, and thus its yield will depend on the degree of H<sup>+</sup> consumption during fluid interactions with surrounding rocks. Calculations using thermodynamic properties for aqueous sulphur species from the SUPCRT database (Johnson et al. 1992; Sverjensky et al. 1997) show that cooling of an SO<sub>2</sub>-bearing aqueous fluid in a closed system from 600 °C to 200 °C yields only partial SO<sub>2</sub> breakdown to sulphide and sulphate, accompanied by progressive pH changes from neutral (pH  $\sim$ 5 at 600 °C) to extremely acidic  $(pH < 2 below 250 \degree C)$ . In contrast, where pH is buffered by silicate rocks (e.g. albite, K-feldspar, muscovite, pH  $\sim$ 5) during fluid ascent and cooling, reaction (11) is shifted to the right due to  $H^+$  consumption, resulting in ~99% breakdown of the initial SO<sub>2</sub> at temperatures below 400 °C.

The behaviour of Au and accompanying metals in these two extreme cases is quite different. This is illustrated in Figure 10, where a model magmatic fluid, containing 10 wt% NaCl equiv., 1 wt% H<sub>2</sub>S, 1 wt% SO<sub>2</sub>, 10 000 ppm Fe, 5000 ppm Cu, and an excess of metallic Au, is cooled numerically in equilibrium or not with the quartz + muscovite/ andalusite + K-feldspar assemblage. The initial fluid composition corresponds to typical salt, sulphur, and metal contents found in the 'supercritical fluid' type of inclusions from major porphyry deposits (Heinrich *et al.* 1999, 2004; Kouzmanov & Pokrovski 2012) and is similar to that adopted in previous modelling studies (e.g. Heinrich 2005).

It can be seen in Figure 10a, b that, in the absence of fluid neutralization by silicate rocks, reaction (11) causes acidification of the cooling fluid, which is favourable for Cu and Fe transport in the form of chloride complexes without significant loss, to temperatures  $\sim 200-250$  °C. In contrast, if the fluid is neutralized by interaction with alkali-alumino-silicate rocks (Fig. 10c, d), >90% of the initial Cu and Fe load will precipitate between 600 °C and 400 °C as magnetite and pyrite + chalcopyrite, which are the main Cu–Fe minerals in high-temperature porphyry stages of potassic alteration (Sillitoe 2010; Kouzmanov &



10

0.1

0.01

200

300

Fig. 10. Concentrations of principal sulphur forms (a, c) and Fe, Cu, and Au (b, d) as a function of temperature in a model cooling magmatic fluid initially containing 10 wt% NaCl, 1 wt% H<sub>2</sub>S, 1 wt% SO<sub>2</sub>, 10 000 ppm Fe, 5000 ppm Cu, and an excess of metallic Au. Thermodynamic properties for S-species and Fe chloride complexes are taken from the SUPCRT database (Jonhson et al. 1992; Sverjensky et al. 1997), whereas those of Cu and Au complexes are, respectively, from Akinfiev & Zotov (2001, 2010) and Table 5 (this study). Panels (a) and (b) show the situation when the fluid cools down in a closed system and is not allowed to react with alkali silicate minerals. Note a dramatic acidification of such a fluid on cooling (shown by pH values on panel (b) due to the SO<sub>2</sub> disproportionation reaction generating sulphuric acid (reaction 11). These acidic pH values are favourable for Fe and Cu transport as chloride complexes to temperatures as low as 300-250 °C; below these temperatures a significant part of Fe, Cu, and S precipitates as pyrite, chalcopyrite, covellite, and native sulphur. Upon cooling, the solubility of gold in the form of  $AuCl_{2}^{-}$  decreases progressively over a wide T range, and its deposition is, thus, not focused to a narrow T window. The calculated Au solubility above 400  $^{\circ}$ C (>10 ppm) is higher than most natural gold concentrations in fluid inclusions, meaning that such SO<sub>2</sub>-bearing fluids are unsaturated with the metal and thus do not precipitate Au. Panels (c) and (d) show the same fluid, cooling in contact with an excess of the quartz + muscovite/andalusite + K-feldspar assemblage that buffers the solution pH between 4.5 and 5.0 in the whole T range. Note a dramatic decrease of  $SO_2$  concentrations below ~500 °C, whereas elevated H<sub>2</sub>S contents (~0.1 mol/kg) are persisting down to 200 °C. These high H<sub>2</sub>S concentrations, coupled with near-neutral pH, are unfavourable for Cu and Fe solubility below 400-350 °C but are favourable for massive Au transport (at ~10 ppm level) to epithermal deposits. Note also a minimum of Au solubility around 450 °C, which corresponds to the high-T Au deposition with Cu in porphyry deposits. These two contrasting scenarios are likely to encompass the range of conditions natural fluids undergo.

600

Pokrovski 2012). However, such a neutralized fluid will be unable to carry significant amounts of Cu and Fe (and Pb, Zn, Ag) to lower-temperature epithermal deposits (<350 °C). The significant transport of these metals to such settings by sulphurrich fluids is, thus, only possible if the fluid does

pH = 5

400

Temperature,

500

°C

300

not lose its acidity when it flows through the rock. It requires the rock to be already altered by an earlier portion of acidic fluid. Such an early acidic fluid prepares a favourable path for subsequent pulses of fluid rich in metals, both by reducing the neutralization capacity of the rock and creating

pH = 5

400

Temperature,

500

°C

600

pH=5

(a)

Sulfur species, mol/kg H<sub>2</sub>O

(**c**)

Sulfur species, mol/kg H<sub>2</sub>O

0.1

0.01

0.00

200

additional permeability due to alteration and partial silicate mineral dissolution (Kouzmanov & Pokrovski 2012).

The behaviour of Au upon the SO<sub>2</sub> breakdown is more complex, because of the change of dominant Au species from chloride (reaction 10c) to hydrogen sulphide (reactions 10a, b, d) with the temperature decrease and the reaction (11) progress. Figure 10 shows that, despite the large differences in Au speciation and solubility-controlling factors between acidic (AuCl<sub>2</sub><sup>-</sup> dominant, Fig. 10b) and neutral  $(Au(HS)_2^-$  dominant, Fig. 10d) fluids, with an excess of sulphur over metals, a magmatic fluid, either buffered or not with rocks, will be able to carry Au at concentrations above 1 ppm to fairly low temperatures (~250 °C) without reaching saturation with the metal. Nevetheless, the potential efficiency of Au precipitation is different for acidic and neutral fluids. In the case of transport as  $AuCl_{2}^{-}$ , and when saturation with the metal is reached, a smooth and regular deposition would occur over a wide T-range (Fig. 10b) and, thus, on a large spatial scale, which is not generally favourable for creating ecomonic Au mineralization. In contrast, the massive transport as  $Au(HS)_2^-$  may occur to temperatures as low as 150-200 °C (Fig. 10d); such fluid would have a far greater potential for Au economic precipitation at such temperatures, when it gets diluted, oxidized, or loses its H<sub>2</sub>S through interactions with Fe-bearing rocks within a narrow temperature and spatial window.

Effect of CO<sub>2</sub>. In addition to sulphur, carbon dioxide  $(CO_2)$  is a very common volatile constituent of fluids and vapours in the majority of gold deposits. It may attain more than 50 wt% in the fluid phase in carbonate-rich contexts such as greenstonebelt and Carlin-type gold, skarn-related gold, or mafic pegmatite Cu-Au and PGE deposits (e.g. Diamond 1990; Phillips & Evans 2004; Goldfarb et al. 2005; Vallance et al. 2009; Hanley & Gladney 2011). In porphyry Cu-Au deposits (e.g. Climax, Butte, Henderson, Bingham, El Salvador), it amounts to 10-20 wt% ( $\sim 5-10 \text{ mol\%}$ ) in deep high-temperature parts corresponding to potassic alteration zones as indicated by analyses of hightemperature fluid inclusions (Rusk et al. 2008, 2011). It is also detected in epithermal Au deposits at the level of a few wt% (André-Mayer et al. 2002).

Much more is known about  $CO_2$  in silicate melts. A detailed review of  $CO_2$  sources, contents, and behaviour in magmas was provided by Lowenstern (2001) and Moore (2008). The two key properties of  $CO_2$  in magmatic systems distinguish this compound from water, chloride, and sulphur: (1) low solubility of  $CO_2$  in most types of silicate melts; and (2) absence of major mineral phases capable of retaining  $CO_2$  in magmatic rocks. These properties are responsible for early degassing of  $CO_2$ from magmas compared to water, salts, and sulphur (Lowenstern 2001) and are likely to be the reason of the relatively modest  $CO_2$  concentrations reported in fluids from intrusion-related Au deposits such as Cu–Au porphyries (Rusk *et al.* 2008) as compared to deposits in metamorphic or sedimentary carbonate-rich rock formations (e.g. Phillips & Evans 2004). Under hydrothermal conditions,  $CO_2$  may affect gold behaviour in different ways, both direct and indirect.

First, the presence of CO<sub>2</sub> affects vapour-liquid phase relationships as compared to a CO<sub>2</sub>-free system. The PVTX properties of the H<sub>2</sub>O-NaCl-CO<sub>2</sub> system are reasonably well constrained today, and physical-chemical models are available for predicting densities of the vapour and liquid phases in this system (e.g. Bowers & Helgeson 1983; Duan et al. 1995; Bakker 2009). These models are, however, not precise enough to quantify the exact T-P conditions of phase transition and composition in the CO<sub>2</sub>-NaCl-H<sub>2</sub>O system, in contrast to the CO<sub>2</sub>-free NaCl-H<sub>2</sub>O system for which far more accurate models are now available (e.g. Driesner & Heinrich 2007; references therein). Nevertheless, existing data indicate that even moderate quantities of CO<sub>2</sub> may significantly extend the vapour-liquid immiscibility domain and increase the pressure of phase separation. For example, the presence of 10 wt% CO<sub>2</sub> in supercritical aqueous fluid containing 10 wt% NaCl at 400 °C will increase the homogenization pressure of the mixture (i.e. the pressure below which two phases, an aqueous vapour and a saline liquid, coexist) from 270 bar (in CO<sub>2</sub>-free, 10 wt% NaCl-H<sub>2</sub>O system) to  $\sim$ 500 bar (in the presence of CO<sub>2</sub>; Bakker 2009). This difference corresponds to more than 2 km of depth under hydrostatic pressure. In the evolution path of the cooling and ascending magmatic fluid, this will allow an earlier (i.e. at greater depth) separation of the vapour and the corresponding Au fractionation into this phase in S-rich systems (section "Vapour transport and vapour-liquid partitioning of gold" above). A more detailed account of phase separation on Au behaviour in different geological settings will be given in the section "Fluid-phase controls on gold ore formation in hydrothermal systems".

Second, because  $CO_2$  is a weak acid (log K of the dissociation reaction  $CO_2 + H_2O = HCO_3^- + H^+$  is -6 to -8 at hydrothermal conditions; Johnson *et al.* 1992), its presence may influence the fluid pH, and thus, Au solubility. Boiling or phase separation lead to an increase in pH of the liquid phase due to preferential partitioning of  $CO_2$  and other acidic volatile components (HCl,  $H_2S$ ,  $SO_2$ ) into the vapour. As a numerical example illustrating this

phenomenon, boiling of a 10 wt% NaCl + 5 wt% CO<sub>2</sub> aqueous solution at 350 °C, resulting in removal of 90% of CO2 into the vapour phase, will increase the pH of the liquid by half an order of magnitude (from 5.0 in initial solution to 5.5 after boiling). If there is still a sufficient amount of H<sub>2</sub>S remaining in the liquid, Au solubility will increase accordingly (Fig. 9a). However, this increase may be attenuated by the departure of H<sub>2</sub>S into the vapour (depending on the extent of boiling), which will tend to decrease Au solubility in the liquid phase (Fig. 9b). Thus, the final effect of boiling is difficult to generalize for Au. In highpressure environments (>2 kbar) typical of Au deposits in metamorphic belts, where boiling does not occur, it was proposed that large amounts of CO<sub>2</sub> in the fluid may buffer pH at a value around 5 and thus allow maintaining relatively high Au concentrations in the form of  $Au(HS)_2^-$  (Phillips & Evans 2004). Such CO<sub>2</sub> buffering control on pH might, indeed, operate at low-to-moderate temperatures ( $\leq$ 350–300 °C), at which water-silicate rock reactions are slow. In contrast, in higher-temperature  $(\geq 400 \ ^{\circ}C)$  salt-rich fluids typical of porphyry or intrusion-related deposits, the effect of CO<sub>2</sub> on fluid pH is likely to be attenuated by rapid fluid equilibration with silicate rocks, so that Au behaviour will be little affected in the presence of  $CO_2$ .

*Third*,  $CO_2$  anionic counterparts, bicarbonate  $(HCO_3^-)$  and carbonate  $(CO_3^{2-})$  ions, may potentially act as direct ligands for 'hard' metals like REE, Sn, Zr, U, Nb, and probably Fe (e.g. Seward & Barnes 1997; Wood & Samson 1998; Pokrovski 2010; references therein). In contrast, base metals, Ag, and Au are not expected to be affected by carbonate complexing both because of their generally low chemical affinity to the 'hard' carbonate ligand (section "General features of gold aqueous chemistry") and the small abundance of carbonate ions in acidic-to-neutral fluids typical of most magmatic-hydrothermal systems.

*Fourth*, when  $CO_2$  is present in large fractions, it may affect solvation phenomena in the fluid phase. Because most metal chloride and hydroxide complexes are solvated by water molecules both in vapour and liquid or supercritical fluid phase (section "Vapour transport and vapour-liquid partitioning of gold" above), lowering H<sub>2</sub>O activity ( $\sim$ mole fraction) in the presence of CO<sub>2</sub> decreases the complex stability and thus, metal solubility. Alternatively, the effect of  $CO_2$  may be explained using the Born electrostatic equation, which uses the dielectric constant of the fluid mixture (see section "Gold chloride, hydrogen sulphide, and hydroxide species in aqueous solution and dense supercritical fluid"). Experimental measurements available for a few oxide and chloride solids in supercritical H<sub>2</sub>O-CO<sub>2</sub> mixtures attest to this

behaviour in a wide range of  $T-P-X_{CO_2}$  conditions (Fig. 11). For example, quartz solubility in a 20 wt% CO<sub>2</sub>-H<sub>2</sub>O fluid at 600 °C and 2 kbar is 1.5 times lower than in pure water at the same T-P(Walther & Orville 1983). A larger effect is observed for ionic compounds, such as AgCl, for example, whose solubility in the form of  $AgCl_2^-$  is lowered by a factor of 3 in a 20 wt% CO<sub>2</sub>-H<sub>2</sub>O fluid compared to pure H<sub>2</sub>O at 400 °C and 1 kbar (Akinfiev & Zotov 1999). A similar decrease is predicted for Au solubility both as AuCl<sub>2</sub> and  $Au(HS)_2^-$  species based on the Born equation of solvation (Fig. 11). By contrast, for neutral and less polar Au-S complexes such as AuHS<sup>0</sup> or AuHS( $\hat{H}_2S$ )<sup>0</sup>, CO<sub>2</sub> would not have a strong influence according to this electrostatic model (Fig. 11).



Fig. 11. Solubility of quartz, silver chloride, and metallic gold in supercritical H<sub>2</sub>O-CO<sub>2</sub> fluids at indicated temperatures, pressures, and pH as a function of CO<sub>2</sub> mole fraction, according to published experimental measurements (Si and Ag) and thermodynamic predictions (Au, this study). Symbols show experimental data for quartz and AgCl(s) in the form of  $AgCl_2^-$  (NM00 – Newton & Manning 2000; WO83 – Walther & Orville 1983; AZ99–Akinfiev & Zotov 1999), whereas straight lines are their least-square linear fits through the data points. Curves for Au species represent calculated concentrations at indicated pH and solution compositions and using the Born model for the Gibbs free energy of solvation (Akinfiev & Zotov 1999) and Born coefficients ( $\omega$ ) for Au species from Table 5:  $\Delta G_{T,P} = \Delta \omega \times (1/\varepsilon_{\text{mix}} - 1/\varepsilon_{\text{water}})$ , where  $\Delta \omega$  is the change in Born coefficient for the corresponding species formation reaction (10a-f), and  $\varepsilon_{water}$  and  $\varepsilon_{mix}$  are the dielectric constants of pure water and the H<sub>2</sub>O-CO<sub>2</sub> mixture, respectively. Note the significant drop of solubility with increasing CO2 content for all species except AuHS whose  $\omega$  value is close to zero (reaction 10b, Table 5).

#### GOLD SPECIATION IN GEOLOGICAL FLUIDS

However, this model does not take into account possible preferential solvation of Au-S non-polar species in a CO<sub>2</sub> solvent (see Pokrovski et al. 2008a, 2009b). Interestingly, the selective solvation capacities of supercritical CO<sub>2</sub> are used in chemical engineering for synthesis and purification of organometallic and organic compounds at moderate temperatures (e.g. Erkev 2000). If such solvation occurs, Au solubility in the form of uncharged sulphide complexes may increase with increasing CO<sub>2</sub> fraction in the fluid. A similar mechanism might influence the vapour-liquid partitioning of gold. The scarce data of Figure 7 in CO<sub>2</sub>-free vapour-liquid systems suggest that volatile Au-sulphur complexes may behave as regular gases and, thus, be enhanced in the presence of CO<sub>2</sub>, both due to increase of the density contrast between liquid and vapour and specific solvation of neutral non-polar molecules like Au-H<sub>2</sub>S complexes by non-polar CO<sub>2</sub> (Pokrovski et al. 2008a). This solvation effect of CO2 awaits, however, experimental confirmation for conditions relevant to hydrothermal gold deposits. Note that it may be efficient only at large CO<sub>2</sub> fractions to change significantly the properties of the aqueous solvent  $(>10-20 \text{ mol}\% \text{ CO}_2)$ , which are common in orogenic gold deposits (e.g. Phillips & Evans 2004). In other types of hydrothermal Au deposits such as porphyry, epithermal, and Carlin, generally characterized by modest  $CO_2$  contents (<10 mol%), the solvation effect on gold transport capacities by fluids is expected to be minor as compared to the other factors discussed above.

Role of arsenic and other metalloids (Sb, Se, Te). In many meso- and epithermal deposits ( $T \leq$  $\sim$ 300 °C), gold is found to be closely associated with arsenian pyrite, arsenopyrite, and sulphide minerals of Sb, Se, and Te (e.g. Boyle 1979; Cathelineau et al. 1989; Arehart et al. 1993; Cabri et al. 2000). Both 'visible' native gold (i.e. particles larger than  $\sim 0.1 \ \mu m$ ) in association with and 'invisible' gold incorporated into these minerals occur. The literature on arsenian pyrite over the last three decades is full of discussions about the chemical and redox state of both As and Au and Au-As chemical and structural relationships in pyrite and arsenopyrite. Based on spectroscopic techniques (SIMS, TEM, Möessbauer, XAS, XPS) and interelement correlations, most studies agree that 'invisible' gold occurs in two chemical states: the elemental form as nanometer-size particles of Au<sup>0</sup>, and chemically bound gold with a still uncertain oxidation state between Au<sup>3+</sup> and Au<sup>1-</sup> (Marion *et al.* 1986; Arehart et al. 1993; Scaini et al. 1998; Simon et al. 1999; Cabri et al. 2000; Palenik et al. 2004; Reich et al. 2005; references therein). Accurate assessment of the Au oxidation state in As-pyrite

using interelement correlations is complicated by the presence of many other elements in far greater concentrations (e.g. Cu, Sb, Ni, Co, Ag, Bi, Se, Te, Reich et al. 2005). The application of direct spectroscopic techniques like XPS or XAS is hampered by their weak sensitivity to low Au concentrations (<100-1000 ppm) and by the presence of As, whose absorption edge energy is very close to that of Au, resulting in peak overlap. Because of these limitations, the wide range of oxidation states suggested for chemically bound Au should be considered with care. The known gold chemistry both in solid and solution implies that the only stable Au oxidation state at hydrothermal conditions is Au<sup>+</sup> (see section "General features of gold aqueous chemistry"). One of the most direct studies of Au in As-pyrite published so far (Simon et al. 1999), using near-edge absorption spectroscopy (XANES), reported the presence both of Au<sup>0</sup> and  $Au^+$  in Au-rich (~1000 ppm) arsenian pyrites from a Carlin-type gold deposit. Chemically bound Au<sup>+</sup> was found to have a nearest coordination number of 2 and 4, based on comparison with Au-bearing standard compounds with known valence and coordination. However, the low signal-to-noise ratio of the EXAFS spectra from that study did not allow identification of the Au first-shell neighbours (S, As, or Fe).

As for arsenic, the majority of spectroscopic, analytical, and thermodynamic studies of arsenian pyrites indicate that As is likely to substitute for sulphur as  $As^{1-}$ , forming a  $Fe(As,S)_2$  solid solution between pyrite and arsenopyrite (e.g. Fleet et al. 1989; Pokrovski et al. 2002b; Reich et al. 2005; Blanchard et al. 2007; Liang et al. 2013; references therein). The only existing exception to these findings is an XPS study of Deditius et al. (2008), who reported the dominant presence of  $As^{3+}$ , likely substituting for Fe<sup>2+</sup>, in pyrites from the Yanacocha gold epithermal deposit. However, because of the high sensitivity of As-pyrites to surface oxidation (e.g. Nesbitt et al. 1995; Liang et al. 2013), care is required in sample preparation for the XPS technique that probes only first 10 of nanometres of the sample surface. In addition, a coordination number of 6 by sulphur for  $As^{3+}$  in the  $Fe^{2+}$  structural site (Deditius *et al.* 2008) contradicts the ubiquitous As<sup>III</sup> coordination number of 3 and corresponding geometries (typically a distorted pyramid) in most solids and aqueous solution (e.g. Borisova et al. 2010; Testemale et al. 2011; references therein). Thus, in the absence of additional investigations, arsenic may be considered most likely to exist as As<sup>1-</sup> in pyrite in the majority of Au deposits. From a thermodynamic point of view, As may be treated as a regular solid solution FeS2-FeAsS (Blanchard et al. 2007) and using the thermodynamic properties of pyrite and

arsenopyrite end-members (Pokrovski et al. 2002b; Perfetti et al. 2008).

The most intriguing feature of gold distribution in the majority of epithermal deposits is its positive correlation with As in pyrite. Total Au concentations vary in a very large range from a few ppb to 1000s ppm in As-pyrites and arsenopyrites. Based on available SIMS, EMPA, XANES, and HRTEM studies cited above, Reich et al. (2005) established an upper solubility limit of chemically bound Au in pyrites from different Carlin-type gold deposits formed between 150 and 250 °C:  $C_{Au} = 0.02 \times C_{As} + 4 \times 10^{-5}$  (mol%). Arsenian pyrites with Au/As ratios below 0.02 have the dominant Au form as Au<sup>+</sup>, whereas those with Au/As molal ratios above 0.02 contain, in addition to Au<sup>+</sup>, significant fractions of Au<sup>0</sup> nanoparticles. From basic thermodynamics postulating that stability domains of most solid solutions extend with increasing temperature, it may be expected that far more gold as Au<sup>+</sup> may be accommodated by arsenian pyrite at elevated temperatures and that part of the Au found in native form in As-pyrite might be due to exsolution phenomena on cooling.

The fundamental reasons for the Au spatial association with As (and accompanying metalloids such as Sb, Se, Te) in sulpharsenides are subjects of continuing debates. Different mechanisms have been proposed to account for the role of As and other metalloids in Au scavenging by pyrite and arsenopyrite. Earlier studies evoked Au transport by the fluid phase in the form of Au–As–S ( $\pm$ Sb, Se, Te) aqueous complexes and their precipitation with ferrous iron (Boyle 1969; Boiron et al. 1989). However, such common precipitation due to the Au-metalloid species breakdown cannot explain the much higher concentrations of As and Sb (wt% level) than Au (ppm level) in pyrites. In addition, although such complexes have been evoked in several studies (e.g. Seward 1973; Nekrasov et al. 1982), they have not been convincingly demonstrated experimentally (see Wood & Samson 1998 for discussion), and the available data reviewed here strongly suggest that hydrogen sulphide and chloride complexes are sufficient to account for Au transport over a wide range of hydrothermal conditions.

Other studies suggested chemisorption of dissolved Au as Au–S/As complexes at As-rich, Fe-deficient sites (Renders & Seward 1989; Mao 1991; Fleet & Mumin 1997; Cepedal *et al.* 2008), electrochemically driven adsorption of negatively charged Au(HS)<sub>2</sub><sup>-</sup> complexes on semi-conducting As-pyrite and arsenopyrite surfaces (Mironov *et al.* 1981; Möller & Kersten 1994), or Au<sup>3+</sup> and Au<sup>+</sup> precipitation on sulphide surfaces due to Au reduction (Maddox *et al.* 1998; Scaini *et al.* 1998). These hypotheses are, however, based mostly on low temperature (<100 °C) experiments, some of them involving Au complexes which are unlikely at hydrothermal conditions (e.g.  $AuCl_4^-$ , see above). These limitations make it difficult to extrapolate these results to the higher temperatures of Au-pyrite formation in nature (>150–200 °C). Different isomorphic substitution models of Au in pyrite were also invoked, including coupled substitutions of  $As^{3+} + Au^+$  for  $2Fe^{2+}$ ,  $As^{3+} + Au^{3+}$  for  $3Fe^{2+}$  (Deditius *et al.* 2008), or  $Cu^+ + Au^{3+}$  for  $2Fe^{2+}$  (Chouinard *et al.* 2005). However, at least some of them are inconsistent with the known As and Au crystal chemistry and redox states at hydrothermal conditions, as discussed above.

Whatever the exact Au state in As-pyrite, native or chemically bound, an important aspect not explicitly expressed in most studies is the role of common precipitation mechanisms of Au and associated metalloids. Thus, the association of native gold  $(Au^{0})$  with arsenopyrite and As-pyrite  $(As^{1-})$  may simply be due to the same reduction process in the hydrothermal fluid in which these elements are commonly transported as Au1+ (chloride, sulphide, other species, see above) and  $As^{3+}$  (As(OH)<sub>3</sub>, Pokrovski et al. 1996a; Perfetti et al. 2008; references therein). Such parallel reduction (Au<sup>1+</sup> to Au<sup>0</sup>, and  $As^{3+}$  to  $As^{1-}$ ) may, for example, occur during fluid interaction with organic-rich sediments common in Carlin-type gold deposits. Similarly, in deposits where gold is late compared to arsenopyrite  $\pm$  pyrite (Heinrich & Eadington 1986; Genkin et al. 1998), native gold deposition on grain boundaries and in cracks of pre-existing  $Fe(As,S)_2$  or FeAsS may easily be explained by minor redissolution of arsenopyrite with formation of As(OH)3 and H2 according to the reaction like

$$FeAsS(s) + 3H_2O + 2H^+ + 2CI^-$$
  
= FeCl<sub>2</sub> + As(OH)<sub>3</sub> + H<sub>2</sub>S + 1.5H<sub>2</sub> (12)

(or equivalent), a process that would act as a local redox trap for gold, as demonstated by thermodynamic calculations (Heinrich & Eadington 1986; Pokrovski et al. 2002b). Other factors such as fluid cooling or boiling are also favourable for Aspyrite/arsenopyrite precipitation together with Au, both in the native or chemically bound state, because of the breakdown of aqueous Au-hydrogen sulphide complexes due to H<sub>2</sub>S scavenging by these minerals (e.g. Velásquez et al. 2014). Similar common precipitation phenomena are likely to be responsible for the close association of Au with other metalloids like Sb, Se, Te, or Bi, which are transported as oxidized hydroxide species in the fluid phase (e.g. Sb(OH)<sub>3</sub>, Pokrovski et al. 2006; Bi(OH)<sub>3</sub>, Tooth et al. 2012), and usually precipitated in more reduced forms (antimonides, native bismuth). These metalloids, if sufficiently abundant, may also form with Au individual solid phases (e.g. Au<sub>2</sub>Bi, AuSb<sub>2</sub>, AuTe<sub>2</sub>, AuAgTe<sub>2</sub>, Pb(Au,Te)S<sub>2</sub>, Ciobanu *et al.* 2006, 2009), alloys and solid solutions (e.g. Bi, Tooth *et al.* 2008), or melts (e.g. Ciobanu & Cook 2006; Wagner 2007), which may scavenge Au from an undersaturated solution. A deeper understanding of the gold-metalloids relationships in hydrothermal systems awaits direct experimental studies at pertinent conditions and development of high-resolution (both in energy and space) *in situ* spectroscopic techniques.

*Colloidal transport of gold.* The chemically 'soft' nature of gold (section "General features of gold aqueous chemistry") allows easy delocalization of outer-sphere electrons and establishment of bonds between gold atoms. This favours the formation of gold clusters and cages involving several Au atoms together with other ligands, leading to formation of gold nanoparticles and colloid-like aggregates, which may stay in solution for prolonged times. This property of gold was used for decorating china and glass articles using 'liquid golds', which are gold multiatomic aggregates with thiolate ligands bound around the Au cluster (Cotton & Wilkinson 1988), and is now widely employed in nanotechnology (e.g. Cobley & Xia 2009).

In natural systems, the common observation of colloform gold with fine-grained quartz and amorphous silica in epithermal deposits (Saunders 1990, 2012; Herrington & Wilkinson 1993; Saunders & Schoenly 1995), and of nanoparticules of gold with clavs in weathering environments (e.g. Hough et al. 2008) incited researchers to suggest that gold was transported in the form of colloids with silica or clays. Such a transport might, indeed, be significant in low-temperature dilute solutions where gold precipitation rates are slow and the absence of electrolytes retards colloid coagulation. The affinity of both Au<sup>+</sup> and Au<sup>3+</sup> for aqueous or colloidal silica and the potential capability of forming stable Au-O-Si bonds may further be inferred using the analogy with other metals. It was demonstated by potentiometry and in situ XAS methods that aqueous silica significantly retards Fe, Al, and Ga hydrolysis and hydroxide precipitation by forming aqueous metal-silica polymeric complexes in solution (e.g. Pokrovski et al. 1996b, 2002c, 2003; references therein). Pokrovski et al. (2002c) showed that the values of stability constants of metal-silicate complexes in solution are linearly correlated with those of the corresponding metal hydrolysis constants. Following this correlation, it is expected that both  $Au^{3+}$  and  $Au^{+}$  might form stable silicate complexes. The exact stability domains of such hypothetical complexes require experimental quantification. By analogy with the low solubility of Au in silicate melts, these Ausilicate species in solution are expected to contribute to Au transport only in low-temperature sulphur- and salt-poor Si-rich environments, probably via specific adsorption and retention of Au on colloidal silica particles.

At elevated temperatures and in salt- and sulphur-bearing hydrothermal fluids, such colloids or Au–Si aggregates are unlikely to survive long enough to allow efficient Au transport, both due to rapid crystallization kinetics and the presence of chloride and sulphide ligands that are sufficient to account for Au transport (see above). The commonly observed gold-quartz association in the majority of hydrothermal deposits is, thus, more easily explained by common depositional mechanisms of both Au and Si upon fluid cooling (e.g. Helgeson & Garrels 1968) or boiling (Seward 1989), rather than by transport as common Au–Si chemical entities.

Hydrocarbons as a potential medium for Au transport. The common association of gold with carbon seams and pyrobitumen in veins and hydrocarbons in fluid inclusions in mining districts such as the Carlin deposits (Nevada) or Witwatersrand (South Africa) tends to suggest that Au was transported directly by hydrocarbons (see Williams-Jones et al. 2009 for an overview). This idea has been verified by Williams-Jones & Migdisov (2007), who measured Au solubility in crude oil and found that up to several 10s ppb of Au can be dissolved at 250 °C. These original experiments point to a potentially significant capacity of hydrocarbons for transporting Au. The exact chemical speciation of Au in such media remains, however, unknown. Following the much higher affinity of Au<sup>+</sup> (which is a stable form in a strongly reducing hydrocarbon medium) for sulphur compared to nitrogen or oxygen (section "General features of gold aqueous chemistry"), it may be expected that Au binds thiol functional groups in oil. To what extent such organic transport may contribute to Au distribution, compared to aqueous hydrothermal fluids, remains to be quantified. It should be noted that Au solubility as  $Au(HS)_2^-$  species in a typical nearneutral aqueous solution at 200-250 °C and sulphur content of 1000 ppm attains easily 100s to 1000s ppb (e.g. Figs 8 & 9). This is at least 1-2orders of magnitude higher than the Au solubility in oil from the available experiments cited above. Thus, Au-hydrocarbon transport and concentration is likely to be restricted to specific petroleumrich and water-poor environments, which might occur in some sedimentary basins. More systematic data on Au-organic matter interactions at elevated temperatures are needed to resolve this issue.

# Comparison of thermodynamic predictions with natural data from porphyry Cu-Au-Mo and related deposits

The gold solubility controls discussed above provide a foundation for interpreting Au concentrations in natural hydrothermal fluids and gold ore precipitation mechanisms in different geological settings. The rapidly growing database of gold and other metals concentrations acquired over the last  $\sim 15$ years, mainly using LA-ICPMS analyses of fluid inclusions from different types of hydrothermal deposits (Yardley 2005; Kouzmanov & Pokrovski 2012; this volume), together with the improved knowledge of Au aqueous thermodynamics discussed above, allows a direct comparison of natural gold contents in hydrothermal fluids with thermodynamic predictions. In this section, we focus on abundant fluid inclusion data on Au from Cu-Au-Mo porphyry and associated epithermal and skarn deposits. Detailed comparisons for other metals are given elsewhere (Kouzmanov & Pokrovski 2012).

Four genetic types of fluid inclusions may be identified in porphyry and associated systems (Kouzmanov & Pokrovski 2012). These types reflect the temperature-pressure evolution in the porphyry environment of a magmatic saline metal-bearing fluid, governed by the phase relationships of the water-salt system: (a) supercritical fluid of moderate salinity ( $\sim 2-10$  wt% NaCl) containing metals and volatiles (CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>) exsolved from the magma; (b) aqueous low-density vapour and (c) hypersaline high-density liquid, both produced by unmixing of the supercritical fluid on cooling and decompression when it crosses the two-phase vapour-liquid boundary of the water-salt system; and (d) low-salinity aqueous solution generated by condensation of the supercritical (a) or vapour-type (b) fluids above and their eventual mixing with meteoric waters in the shallow epithermal environment of porphyry systems. Thus, the characteristic parameters that distinguish among these types are the temperature of homogenezation  $(T_h)$  and salinity (NaCl wt% equivalent) as derived from microthermometric measurements of inclusons. In addition, recent improvements of LA-ICPMS techniques allowed direct analyses of sulphur contents in these fluid inclusions (Guillong et al. 2008; Seo et al. 2009, 2011, 2012; Catchpole et al. 2011, in press). This provides new constraints on the impact of sulphur on Au behaviour based on thermodynamic calculations of Au speciation and solubility.

Gold concentrations measured in the four types of inclusions from porphyry and associated deposits are plotted v.  $T_h$ , chlorinity (NaCl wt% equivalent),

and sulphur content (ppm) in Figure 12a-c. Note that the temperature of homogenization provides an estimate of the minimum temperature of entrapment. For coexisting liquid-vapour 'boiling' assemblages of inclusions, a unique estimate of temperature and pressure of entrapment is possible using the well-known PVTX properties of the H<sub>2</sub>O-NaCl system (e.g. Driesner & Heinrich 2007); in all other cases, a correction is required for the true temperature of entrapment. This correction (towards higher temperatures) may be estimated using different geothermometers when available (trace element- or stable isotope-based). For the supercritical and low-salinity types of fluid inclusions shown in Figure 12a, this correction usually does not exceed 50-100 °C, implying that the entrapment temperature is usually higher that the observed homogenization temperature. However, this should not change dramatically the main trends in Au solubility discussed below. Another caveat when comparing Au contents in natural fluid inclusions with thermodynamic predictions of Au solubility is that many natural fluids are probably undersaturated with metallic gold because of the generally low abundance of this trace metal. As a result, Au contents measured in natural fluid inclusions may not always be as sensitive to variations of T, P, mS, or salinity as Au solubility itself (i.e. Au solution concentrations in equilibrium with the metal). In addition, Au may also enter sulphide minerals as chemically bound or nano-particulate Au, whose solubility is different from that of bulk crystalline Au. Nevetheless, the solubility trends discussed below allow one to place rough limits on the capacity of natural fluids to transport Au in a given natural setting and to identify the most apparent trends.

The measured Au concentrations in Figure 12 are compared with the calculated values as a function of T, salinity, and  $H_2S$  concentration in equilibrium with metallic gold and using the thermodynamic properties of Au hydroxide, chloride, and hydrogen sulphide species recommended above (Table 5). The chosen redox and acidity conditions are typical of porphyry systems as inferred from mineral associations and wall-rock alteration patterns. The assemblage magnetite-hematite was chosen as a proxy for the oxygen fugacity (Einaudi et al. 2003), and the pH was constrained between 3 and 5 which corresponds to the different extent of fluid buffering by alkali alumino-silicate assemblages common in porphyry deposits in a wide temperature range (Meyer & Hemley 1967; Reed 1997). Acidic pH usually corresponds to fluids represented by the low-salinity aqueous type of inclusions in high-sulphidation epithermal deposits; they are produced by condensation of the magmatic HCl- and SO<sub>2</sub>-bearing vapour or



**Fig. 12.** Gold concentrations measured in four types of fluid inclusions from porphyry and associated deposits (indicated by symbols) as a function of (**a**) temperature of homogenization, (**b**) salinity, and (**c**) measured sulphur concentrations, and their comparison with calculated gold solubility (curves) at indicated conditions of temperature, pH, sulphur content, salinity, and redox potential (redox buffers are defined in Figs 8 & 9). Thermodynamic properties of Au species are from Table 5, those of solid phases and major fluid constituents and sulphur forms are from the SUPCRT database. For data sources in panels (a) and (b), see the caption of Figure 5; data in panel (c) are from Guillong *et al.* (2008), Seo *et al.* (2009, 2011, 2012), and Catchpole *et al.* (2011, in press).

supercritical fluid phase generating acids on cooling (see section "Major parameters controlling Au transport and precipitation in hydrothermal fluids" above). Near-neutral pH values (close to 5) are typical of high-temperature magmatic fluids, which equilibrate with alkali-silicate rocks. Sulphur concentrations in these calculations correspond to those from fluid-inclusion analyses from porphyry (Seo *et al.* 2009, 2011, 2012) and high-to-intermediate sulphidation epithermal (Catchpole *et al.* in press) deposits; they typically range from 0.1 to 1 wt% (Fig. 12c).

It can be seen in Figure 12 that analysed natural gold concentrations span from  $\sim 0.03$  to  $\sim 25$  ppm for the available dataset and are independent (within the data scatter) of the inclusion type, temperature, and salinity. The absence of clear temperature dependence of natural Au concentrations agrees with the calculated Au solubility trends with sulphur concentrations at 0.1 wt% at pH 5 (Figs 8a & 12a). Higher sulphur contents, corresponding to an average value of the available analyses of fluid inclusions (0.7 wt%), yield Au solubilities at nearneutral pH higher than the majority of inclusions. More acidic pH (pH 3-4) and more reducing conditions (e.g. NNO buffer) would lead to lower Au calculated solubilities than those shown by the curves in this figure, better corresponding to the natural analyses. Note that Au solubilities calculated assuming sulphide buffering with the major Fe-bearing minerals (e.g. PPM buffer) yield Au concentrations below 400-450 °C much lower than the natural contents. This strongly suggests that most epithermal fluids transporting Au (corresponding to the low-salinity aqueous type of inclusion in Fig. 12a) were Fe-poor and exhibited no significant loss of sulphur during their interactions with rocks. At temperatures higher than 500 °C, most fluids are undersaturated with metallic gold, consistent with the common lack of Au deposition above 500 °C in porphyry systems.

The independence of Au natural contents of salinity (Fig. 12b), which contrasts with all base metals (see Kouzmanov & Pokrovski 2012), is consistent with a weak fraction of Au chloride species at nearneutral H<sub>2</sub>S-rich fluids, particularly at temperatures below 450–500 °C (Fig. 8d). The large majority of Au fluid inclusion analyses are within the range of Au solubility calculated as a function of NaCl with S contents between 0.1 and 1 wt% at pH 5. However, it should be noted that direct analytical data on sulphur contents are still very limited and at present only available for few porphyry and one epithermal deposit. More data on S concentrations are, thus, necessary for robust interpretion of Au concentration trends.

Measured gold concentrations in all types of inclusions where S contents are available do not

show clear correlations with sulphur (Fig. 12c), but the data scatter, together with simultaneous variations of acidity and temperature, may obscure the trends. Absolute sulphur concentrations measured so far in fluid inclusions at temperatures above 400 °C (>1000 ppm) are consistent with the solubilities of the major iron and copper sulphides (e.g. Fig. 8b). At lower temperatures, however, these solubilities are very low, and the elevated sulphur concentrations, found in fluid inclusions of the 'aqueous solution' type typical of epithermal deposits, indicate that these fluids lack iron (and copper) compared to sulphur. This points to the origin of such fluids from a condensed Fe-deficient but S-rich vapour phase, which is a widely accepted modern scenario of epithermal deposit formation (Heinrich 2005). This condensate should be acidic (pH < 3-4) to be able to transport Cu, Fe, Ag, Pb, and Zn, which are all present at elevated concentrations in this fluid type (100s-1000s ppm, Kouzmanov & Pokrovski 2012). The high fluid acidity is consistent with the dissociation of volatiles such as HCl and the disproportionation of SO<sub>2</sub> to H<sub>2</sub>S and sulphuric acid on cooling (see section "Major parameters controlling Au transport and precipitation in hydrothermal fluids"). Figure 12c compares measured Au contents with calculated Au metal solubilities as a function of sulphur concentration at different T and pH reflecting the progressive acidification of the magmatic fluid on cooling (e.g. Sillitoe 2010). It can be seen that the calculations account reasonably well for the Au contents within the typical pH, T, and redox potential ranges of porphyry deposits, with only a few exceptions for particularly Au-rich moderatetemperature 'aqueous-type' fluid inclusions, which appear to be supersaturated with Au metal. At present, it is difficult to quantitatively account for these differences, which may be due to (1) uncertainties intrinsic to the determination of the true entrapment temperature, (2) less acidic pH than those used in the calculations in Figure 12c, (3) colloidal Au transport (section "Major parameters controlling Au transport and precipitation in hydrothermal fluids") and/or heterogeneous entrapment of Au nanoparticles (e.g. Pudack et al. 2009; Kouzmanov et al. 2010), and (4) omission of other Au species in calculations. The latter issue is particularly relevant in view of a recent discovery of polysulphide forms, such as  $S_3^-$ , in S-rich acidic-to-neutral fluids, which might account both for enhanced Au transport as direct complexes with  $S_3^-$ , and increased solubility of other metal sulphide minerals in such solutions due to the consumption of  $H_2S$  to form  $S_3^-$  (Pokrovski 2011; Pokrovski & Dubrovinsky 2011). Additional experimental data on Au speciation in S-rich fluids coupled with systematic analyses of S concentration and chemical state in natural fluid inclusions from porphyry-epithermal environments will confirm or reject this hypothesis.

# Fluid-phase controls on gold ore formation in hydrothermal systems

During their evolution in the crust, magmatic, hydrothermal, or metamorphic Au-bearing fluids undergo five major processes causing gold and accompanying metals redistribution and deposition: cooling, decompression, phase separation (or boiling), interaction with rocks, and mixing with external waters. All of them are interconnected and may be overprinted on one another or act in parallel. The improved knowledge of both Au natural concentrations and chemical speciation in the liquid and vapour phases may help to better estimate the impact of each of these processes on gold precipitation in mineral deposits in different geological environments. Below, we discuss major consequences of each of these processes on Au transport and deposition with examples of different gold deposit types.

### Cooling

Temperature is believed to be the most direct factor that influences mineral solubility and, thus, metal transport and precipitation. Helgeson & Garrels (1968) were among the first to suggest, based on thermodynamic modelling, that cooling of an acidic saline fluid is an efficient mechanism of Au deposition with quartz and pyrite in veins. Since then, the effect of cooling was demonstrated for base metals (Cu, Mo, Fe, Zn, Pb) in different geological settings ranging from porphyry Cu-Au to VMS Zn-Pb deposits. For example, cooling of a single-source magmatic-hydrothermal fluid in a relatively small T interval (450–350  $^{\circ}$ C) was likely the main cause of copper deposition in Cu-Au-Mo porphyry deposits such as Bingham (Landtwing et al. 2005), Bajo de la Alumbrera (Ulrich et al. 2001), and Butte (Rusk et al. 2004), and Cu-Zn-Pb epithermal deposits such as Morococha (Catchpole et al. 2011, in press). These and other natural observations are consistent with the general temperature dependence of metal sulphide mineral solubility that decreases dramatically with temperature decrease in a saline fluid (Hemley & Hunt 1992; Hemley et al. 1992; Kouzmanov & Pokrovski 2012).

The effect of T on gold deposition is, however, less straightforward than for other metals. As was shown in the section "Major parameters controlling Au transport and precipitation in hydrothermal fluids," gold behaviour in a cooling fluid is primarily

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dependent on changes in reduced sulphur concentration. With an excess of ferrous iron (and copper) over sulphur in the fluid, pyrite  $\pm$  chalcopyrite precipitation leading to sulphur removal from the fluid will cause Au precipitation. Thus, cooling of a magmatic saline fluid rich in Fe  $\pm$ Cu, such as those from porphyry systems, is expected to deposit Au together with Cu and Fe sulphides. This is likely to happen in high-temperature parts of porphyry systems (Sillitoe 2010), as well as in most Cu-Zn-Pb deposits on the seafloor (Candela 2004), where the rapid cooling of the fluid scavenges all H<sub>2</sub>S in the form of metal sulphides, causing Au to precipitate. In contrast, vapour-like fluids produced by phase unmixing and enriched in H<sub>2</sub>S over Fe and Cu are expected to carry Au in the form of volatile sulphide species down to 150-200 °C without precipitation (e.g. Fig. 8b). These conditions are likely to operate in highsulphidation epithermal deposits spatially related to porphyry systems (e.g. Heinrich et al. 2004).

Cooling does not only cause metal sulphide precipitation in porphyry systems; it is also accompanied by large changes in sulphur speciation itself in the fluid phase, which consists of SO<sub>2</sub> disproportionation into sulphate and sulphide (see reaction 11, Fig. 10). The extent of fluid pH buffering by alkali silicate rocks will determine the amplitude of Cu, Fe, and Au transport and precipitation on cooling. In addition, the interplay between the initial fluid redox, S, Cl, and major metal concentrations may have different effects on Au behaviour in different deposits (e.g. Heinrich 2005). This uncertainty is superimposed with another major unknown of Au aqueous chemistry, the existence or not of dissolved complexes with sulphur forms other than H<sub>2</sub>S, such as SO<sub>2</sub> or polysulphides (Pokrovski et al. 2008a, 2009b), which may be important in oxidizing environments typical of porphyry deposits.

#### Decompression

The second change the cooling and ascending fluid undergoes is pressure decrease. Although, the most obvious effect of decompression is phase separation (which will be discussed in the following subsection), pressure decrease in a single-phase fluid may also affect Au v. Cu solubility. As was shown in the section "Major parameters controlling Au transport and precipitation in hydrothermal fluids" pressure changes affect Au solubility indirectly, mostly by changing H<sub>2</sub>S concentration in the fluid (Fig. 8c). However, accurate quantification of this effect on Au solubilities is difficult at present because of the lack of experimental data, particularly for lowdensity vapours and supercritical fluids. Thus, only a few qualitative observations can be done here. Boyle (1969) argued, based on structural observations, that pressure changes due to rock faulting and cracking are far more significant than are changes in temperature for depositing gold and quartz, by saying that 'if there is no dilatancy, there is no deposit.' Recent thermo-mechanical modelling of the effect of earthquakes on goldquartz vein formation (Weatherley & Henley 2013) suggests that faults opening during seismic events result in a large fluid pressure drop owing to creation of empty space, which, in turn, yields rapid and efficient quartz, gold, and other metals precipitation via so called 'flash vapourization' of the fluid.

Pressure was suggested to influence Cu/Au ratios in porphyry deposits. Murakami et al. (2010) compiled Cu/Au ratios from 50 porphyry  $Cu \pm Au \pm Mo$  deposits and noted that these values have large variations, from  $10^3$  to  $10^6$ , but increase with increasing depth and pressure of ore deposition. This was explained by earlier precipitation of chalcopyrite compared to gold from a cooling moderate-salinity fluid, whereas Au is stabilized in low-P, low-density fluids as sulphide complexes. Landtwing et al. (2010) suggested that deposit-scale variations of Cu/Au ratios in the Bingham ore are due to different fluid paths, under slightly different pressure-density regimes, of a common input fluid in the central part and the periphery of the porphyry stock. Thus, in the central zone of the orebody, characterized by abundant fracturing and higher permeability (Gruen et al. 2010), the magmatic fluid expands under hydrostatic pressure and ore deposition occurs from a vapour-like fluid enriched in S and Au but impoverished in Cu, compared to the input magmatic fluid. In the deeper peripheral zones, by contrast, this input magmatic fluid cooled at higher pressure and, thus, underwent less contrasting phase separation, leading to brine and vapour phases with compositions closer to the original magmatic fluid. This resulted in Cu/Au ratios in precipitated ore similar to those in the fluid. Similar Cu-Au zonations are observed in other porphyry Cu-Au deposits (e.g. Batu Hijau, Indonesia, Arif & Baker 2004). However, it should be kept in mind that pressure evolution in porphyry deposits is easier to trace than those of the other parameters and that the pressure and temperature decrease and associated changes (pH, sulphur speciation) occur all together; as a result, it is difficult at present to rigourously identify the contribution of pressure itself on Au distribution.

#### Phase separation

The third key process, ultimately related to the temperature and pressure decrease the fluid may undergo when ascending to the surface, is boiling

or phase immiscibility. This phenomenon is manifested in magmatic-hydrothermal systems by coexisting liquid- and vapour-rich fluid inclusions. In the deep porphyry environment, phase separation results in condensation of a hypersaline liquid from the dominant low-salinity vapour phase (Heinrich 2007; Richards 2011), whereas in the epithermal environment, the phase separation occurs by boiling of the dilute aqueous liquid with formation of vapour bubbles. The effect on gold transport and deposition in these two cases is different.

As shown in the section "Vapour transport and vapour-liquid partitioning of gold" phase separation at high T-P results in a contrasting fractionation of metals, with As, S, and Au (and partly Cu) enriched in the vapour phase compared to Fe, Zn, Pb, Ag (Fig. 5). This enrichment was believed to generate fluids forming Au-Cu epithermal deposits in near-surface environments (Heinrich 2005), when the vapour phase condenses into S-bearing aqueous solution transporting Au at relatively low temperatures (see above). Such conditions may occur in high-sulphidation Cu-Au (Hedenquist et al. 1993, 1998; Heinrich et al. 2004) and probably Carlin-type Au (Muntean et al. 2011) deposits, spatially associated with magmatic intrusions, which may provide a source of vapour. However, alternative formation scenarios, for Carlin-type Au deposits, suggesting metamorphic breakdown of sedimentary pyrite hosting Au and other metals and subsequent concentration and deposition of Au by hydrothermal processes involving rock sulphidation, cannot be excluded (e.g. Large et al. 2011; references therein). Whatever the source of gold, sulphur plays a key role in the Au budget in the brine and vapour phases. Note that the mass of the vapour produced during magmatic fluid evolution largely exceeds that of the brine in porphyry deposits, with typical vapour/brine mass ratios between 4 and 9 (e.g. Hedenquist et al. 1998; Landtwing et al. 2010; Lerchbaumer & Audétat 2012). Adopting a reasonable average value of 5 for the vapour-liquid partitioning coefficient of Au in a S-rich acidic porphyry environment (Figs 6 & 7; Pokrovski et al. 2008a), the vapour phase formed upon unmixing of the ascending magmatic fluid will concentrate more than 90% of the total Au. In contrast, adopting a recently recommended  $K_{\text{vabour/liquid}}$  value of 0.10-0.15 for Cu at the same conditions (Lerchbaumer & Audétat 2012), the brine and vapour phases will likely carry comparable copper amounts. Thus, these differences in Au and Cu distribution may also explain the Au/ Cu zonations apparently caused by decompression, as discussed in the previous subsection.

In low-temperature/pressure epithermal environments (<350-300 °C), the density of the vapour phase is too low for significant Au

partitioning into the vapour phase (Figs 6 & 7). The main effect of liquid boiling under such conditions is removal of H<sub>2</sub>S and CO<sub>2</sub> into the vapour. This leads to breakdown of Au-hydrogen sulphide complexes and may result in gold precipitation in veins of bonanza zones (e.g. Saunders & Schoenly 1995; Simmons et al. 2005). Seward (1989) showed, using thermodynamic modelling, that, in active geothermal systems such as Broadlands-Ohaaki (New Zealand), boiling and conductive cooling of the deep  $Au(HS)_2^{-}$ -bearing fluid at  $\sim 290$  °C in an open system, allowing removal of the H<sub>2</sub>S-bearing vapour phase, induces precipitation of most of the Au over a ~15 °C interval. The efficiency of the vapour removal strongly depends on the permeability of the system. Focused fluid flow and efficient Au deposition induced by boiling were suggested to be two key factors for the formation of large Au epithermal deposits, based on studies of active geothermal systems (e.g. Simmons & Browne 2007). In addition, boiling results in the liquid becoming more alkaline (pH increase) due to a loss of CO<sub>2</sub>, which, in turn, may lead to precipitation of galena, sphalerite, chalcopyrite, pyrite, and argentite (see section "Major parameters controlling Au transport precipitation in hydrothermal and fluids" for detailed discussion of the CO<sub>2</sub> effect). For example, Velásquez et al. (2014) showed that boiling of a CO<sub>2</sub>-bearing fluid at  $\sim$ 250 °C induced by faulting events in the El Callao mining district (Venezuela) was likely responsible for the common precipitation of Au and As-bearing pyrite. Boiling at temperatures below 300 °C is likely to be responsible for Au, Ag, and associated base metal sulphides deposition in low-sulphidation epithermal deposits (e.g. André-Mayer et al. 2002).

#### Fluid-rock interactions

The fourth event accompanying the evolution of hydrothermal fluids is their interaction with wall rocks. This leads primarily to changes of pH and sulphide content, which result in Au precipitation. This was inferred from field observations more than 40 years ago, by recognizing that slow fluid 'diffusion' through the rock is one of the principal mechanisms of formation of most Au deposits (Boyle 1969).

In porphyry and related settings, fluid-rock interactions are expressed as alteration zonation centred on the fluid source and propagating into the surrounding rocks (Sillitoe 2010). Note that pH neutralization alone of an acidic S-rich fluid is not expected to decrease Au solubility (Fig. 9a), but it leads to precipitation of major metals (Fe, Cu, Zn, Pb) as sulphides resulting in removal of reduced sulphur from the fluid and thus destabilization of Au-hydrogen sulphide complexes. Skarn deposits with a common metal zonation from proximal  $Cu \pm Au$  to distal Zn + Pb zones, resulting from a combination of temperature decrease and neutralization of the acidic magmatic fluid by carbonate rocks, are a good example. Carbonate sedimentary Au deposits in distal parts of porphyry systems (e.g. Cunningham *et al.* 2004) are another example of far-field flow of ore fluids accompanied by rock dissolution of carbonates and the resulting pH rise.

Fluid interactions with an Fe<sup>II</sup>-rich rock also act as a sink for hydrogen sulphide by precipitation of pyrite  $\pm$  pyrrhotite. This efficient H<sub>2</sub>S consumption from the fluid shifts reactions (10a, b, & c) to the left, leading to gold precipitation. Mafic rocks rich in ferrous iron are, thus, an excellent sink for H<sub>2</sub>S. High Cu and Au grades are associated with mafic rocks, such as at the Oyu Tolgoi and Resolutions deposits (see Sillitoe 2010). Wall-rock sulphidation is the primary control on metal deposition in deep and high-temperature orogenic gold systems; in addition, with decreasing depth of formation, phase separation favoured by significant CO<sub>2</sub> content may also contribute to Au precipitation (e.g. Mikucki 1998; references therein).

#### Fluid mixing

The fifth phenomenon is mixing of two fluids with distinct temperature, acidity, or composition, which may induce gold ore formation in nearsurface crustal settings such as seafloor hydrothermal systems and Mississippi Valley-type deposits (Candela 2004). Mixing of gold-bearing hydrothermal fluid with meteoric waters leads primarily to dilution, oxidation, and additional cooling. These phenomena, together with boiling, discussed above, are likely to be responsible for Au deposition in some low-sulphidation epithermal deposits similar to meteoric-water-dominated active geothermal fields (e.g. Simmons et al. 2005). Mixing between fluids of contrasting acidities is more difficult to evaluate for Au. Such a mixing is expected to have an indirect influence, for example, leading to precipitation of Fe and other metal sulphides with increasing pH and resulting in uptake of reduced sulphur. For example, thermodynamic modelling indicates that mixing of an acidic Au-Ag bearing fluid with meteoric alkaline waters was the main cause of Au-Ag sulphide deposition in the epithermal Yunoe deposit, Russia (Pal'yanova & Savva 2009). Mixing between seawater and magmatic fluid may also cause Au and Cu precipitation in IOCG deposits (e.g. de Haller & Fontboté 2009). By contrast, there is no robust evidence for incursion of groundwater into deep high-temperature porphyry Cu-Au orebodies, and many studies (e.g. Hedenquist et al. 1998; Ulrich et al. 2001; Watanabe & Hedenquist 2001; Harris & Golding

2002; Seedorff & Einaudi 2004) show that most porphyry fluids have a dominantly magmatic component. Similarly, there is no evidence of significant fluid mixing in deep orogenic Au deposits (Mikucki 1998).

#### Conclusions

This paper has presented an overview of gold chemical speciation, solubility, and partitioning in aqueous fluids and vapours over the wide range of temperature and pressure conditions of the Earth's crust. The data acquired using experimental and modelling approaches show that aurous gold  $(Au^+)$ is by far the most stable redox form of Au both in solids and fluids in the majority of hydrothermalmagmatic and metamorphic settings. The major Au aqueous complexes in hydrothermal fluids are chloride and hydrogen sulphide species,  $AuCl_2^-$ ,  $Au(HS)_{2}^{-}$ , and AuHS, for which robust thermodynamic data are available within the HKF model in a wide T-P range. These data allow accurate predictions of Au solubility and quantification of different fluid parameters (e.g. temperature, pressure, salinity, redox, acidity, sulphur content) on Au mobility and precipitation in hydrothermal fluids.

In S-rich (>0.5-1.0 wt% S) hydrothermal and metamorphic fluids, Au might also form soluble complexes with polysulphides. Sulphide, chloride, and/or hydroxy-chloride forms of Au are also responsible for its transport by the low-density vapour phase, but their exact stoichiometry and stability remain poorly constrained. In magmatic fluids, Au may form species with alkali metals, chloride, and reduced sulphur. Gold is the most volatile economic metal in the H<sub>2</sub>O-salt-sulphur two-phase system, with vapour/liquid partitioning coefficients ( $K_{vapour/liquid}$ ) up to 10, likely due to complexing with reduced sulphur. In silicate melt-aqueous fluid systems, Au largely partitions into the aqueous fluid ( $K_{\rm fluid/Si-melt} \approx 1000$ ) and/ or into iron/copper sulphide melts relative to the silicate melt ( $K_{\text{FeS/Si-melt}} \approx 1000-10000$ ). Thus, reduced sulphur appears to exert a key influence on Au behaviour in melts, fluids, and vapours.

Comparison of thermodynamic predictions with natural Au and S concentrations recently measured in fluid inclusions from porphyry deposits in different fluid types generated through the evolution of magmatic fluid (single-phase fluid, vapour, brine, aqueous solution) further confirms the key role of dissolved sulphur to account for the observed natural Au concentrations (typically between 0.1 and 10 ppm). In most cases, elevated sulphur concentrations (>0.1 wt%) are necessary to concentrate and transport Au by the fluid phase in porphyry-epithermal settings. Changes in fluid

acidity and in the extent and rate of interactions with the surrounding rocks during fluid ascent and cooling account reasonably well for the Au contents observed in natural fluid inclusions.

Although Au fractionation and deposition in the crust may be caused by different overlapping processes, it is ultimately related to the behaviour of sulphur. Thus, changes in sulphur availability, redox state, and speciation in the fluid during its evolution are directly reflected on the gold fate. Amongst the main phenomena geological fluids undergo, cooling accompanied by decompression and water-rock interactions is likely to be the major cause of Au (and associated metals) deposition and fractionation in most high-temperature porphyry contexts. Fluid immiscibility that occurs in these environments may significantly impact the Au budget by concentrating it in the sulphur-rich vapour phase, which is likely to provide a source of Au for shallower epithermal deposits. Fluid-rock interaction such as sulphidation and neutralization are likely to be the main cause of Au deposition in orogenic and skarn deposits. Boiling and mixing with meteoric waters may contribute to Au deposition in shallow, low-temperature epithermal settings. In many cases, Au transport and deposition is also conditioned by the amount of more abundant base metals (Fe, Cu, Zn) in the fluid, which compete with Au for sulphur. This competition may be critical in magmatic-related deposits. In contrast, the direct effect of other trace elements (As, Se, Te) on the Au transport and precipitation seems to be minor; their close association with Au in most settings may adequately be explained by common sources and depositional processes. The effect of CO<sub>2</sub> on Au behaviour is to enhance vapour-brine separation, which yields to changes in sulphur content and pH of the liquid phase in epithermal low-temperature environments, and direct Au partitioning onto the vapour in high-temperature magmatic-related deposits.

#### **Remaining gaps and future directions**

This study has also highlighted that, in spite of significant progress in understanding the composition and properties of Au-transporting geological fluids at elevated temperatures and their thermodynamic modelling, much remains to be done. This concerns analytical, experimental, and theoretical fields of research on gold whose major near-future challenges are briefly outlined below.

#### Analytical

A number of analytical challenges for fluid inclusions, which are the only direct witnesses of

natural fluids, remain to be addressed. If Au concentrations can now be routinely analysed in hydrothermal fluid inclusions at levels of a few ppm by modern LA-ICPMS machines (Seo et al. 2009), the situation is different for sulphur, which is the primary element controlling Au behaviour in magmatic-hydrothermal systems. Sulphur remains one of the most poorly quantified major fluid components. Only a few studies have measured S content in individual fluid inclusions using LA-ICPMS (Guillong et al. 2008; Seo et al. 2009, 2011; Catchpole et al. 2011, in press). Such total sulphur analyses should be coupled with in situ spectroscopic determination of the abundances of different sulphur species using in situ micro-Raman spectroscopy (e.g. Giuliani et al. 2003), and X-ray absorption and emission spectroscopy (e.g. Métrich et al. 2009; Alonso Mori et al. 2010). New developments of microanalytical techniques based on standardless approaches for XAS (e.g. Cauzid et al. 2007) and LA-ICPMS (Borisova & Gouy pers. comm.) should allow quantification of Au and associated metals in water-poor C-O-H fluid inclusions and gas bubbles. A better account of possible fluid-inclusion post-entrapment modifications due to selective metal diffusion through the host quartz (e.g. Zajacz et al. 2009; Lerchbaumer & Audétat 2012) is also essential for robust interpretation of Au, Cu, and Ag concentrations in the fluid.

In contrast with porphyry-style deposits for which a large dataset on fluid compositions has been produced for many metals including gold (e.g. Kouzmanov & Pokrovski 2012), the information on Au content in fluids from shallow, low-to-moderate temperature environments like epithermal and Carlin-type deposits is fragmentary. In such settings, a recently developed method combining nearinfrared microscopy with LA-ICPMS may allow direct analyses of metal-precipitating fluids in inclusions hosted by opaque ore minerals such as enargite, wolframite, stibnite, sphalerite, tetrahedrite, and pyrite (Kouzmanov et al. 2010). This would allow verifying the broadly accepted paradigm that gangue (quartz, calcite) and associated ore (metal sulphide) minerals are cogenetic. For example, recent LA-ICP-MS analyses of sphaleritehosted fluid inclusions from Mississippi Valley-type zinc-lead deposits indicate that sulphide ore minerals precipitated from anomalously metal-rich batches of fluid compared to those precipitating the gangue minerals (Wilkinson et al. 2009).

Because Au is commonly associated with sulphide minerals such as pyrite and chalcopyrite and enters their structure both as chemically bound and nano-particulate metal, quantification of contents and redox states of Au and associated trace metals (e.g. As, Se, Te) in these minerals is required for estimating Au budget in a deposit, understanding Au precipitation mechanisms, and developing efficient extraction procedures. Such *in situ* analyses should be achieved via a combination of complementary microanalytical and spectroscopic tools such as LA-ICPMS, SIMS, and XAS.

#### Experimental

The analytical issues discussed above should advance in parallel with speciation and solubility experiments in model laboratory systems under controlled conditions that nature does not offer. If, in volcanic vapours, H<sub>2</sub>S and SO<sub>2</sub> are undoubtedly the major sulphur species at 1 bar over a wide temperature range, sulphur speciation in dense aqueous fluids and silicate melts is quite different and represent the major gap of our knowledge. The recent discovery of a polysulphide sulphur form in S-rich fluids, the trisulphur ion  $S_3^-$ , which is stable in aqueous solution above 250-300 °C over a wide pressure range (Pokrovski & Dubrovinsky 2011; Pokrovski & Dubessy 2012; Jacquemet et al. in press), might affect our interpretation of both sulphur behaviour and its control of Au in S-rich fluids typical of porphyry and orogenic deposits. In situ spectroscopic approaches (e.g. Raman) are necessary to better constrain the stability domain of  $S_3^-$  and other intermediate sulphur forms (e.g. other polysulphides, SO<sub>2</sub>, and sulphites). Once it is achieved, specially designed solubility and spectroscopy (e.g. XAS) experiments in systems where such sulphur species are abundant should allow quantifying their effect on the solubility and transport of Au and other sulphur-loving metals (e.g. Cu, Mo, Pt).

Few experimental data are available on Au speciation and partitioning in vapour-brine-silicate melt systems (e.g. Lerchbaumer & Audétat 2012) and on Au solubility in the major sulphide minerals such as chalcopyrite, bornite, pyrhhotite, and pyrite at temperatures from 500 °C to 700 °C, typical of porphyry Cu–Au deposits (e.g. Simon *et al.* 2000). This lack prohibits a quantitative account of Au vapour-phase transport and Au budget in such settings. Little is known about Au solubility and speciation in deep metamorphic fluids (>2–4 kbar, >500 °C) enriched in sulphur produced by pyriteto-pyrrhotite breakdown (e.g. Tomkins 2010).

The common association of gold with arsenic and other metalloids (Sb, Bi, Se, Te) in hydrothermal deposits might indicate the existence of Au complexes with these elements ( $\pm$  sulphur) in the fluid phase. At present however, this hypothesis remains speculative owing to the absence of quantitative data on the stoichiometry and stability of such species. Acquisition of such data would represent a formidable challenge for experimentalists both because of the extreme toxicity of certain metalloids (Se and Te) and poor knowledge of their own speciation in aqueous solution and gas phase. An additional issue here is the insufficiently constrained thermodynamic properties of Au-bearing As-Sb-Bi-Te-Se-S minerals (e.g. Au<sub>2</sub>Bi, AuSbS<sub>2</sub>, AuTe<sub>2</sub>, AuBiS<sub>2</sub>), which may host a significant part of gold in epithermal deposits. The mechanisms and driving forces of Au scavenging by these chalcogenide minerals during precipitation would be another formidable task for courageous experimentalists.

Another essential experimental need is to better understand the effect of  $CO_2$  on gold transport. Although recent studies (e.g. Pokrovski *et al.* 2008*a*; Hanley & Gladney 2011) evoke enhanced transport of Cu, Au, Pd, and Ni by  $CO_2$ -rich fluids or vapours, yet there is no sound physical-chemical interpretation of this potentially important phenomenon because of a lack of experimental data on ore metal solubility in  $CO_2$ -rich fluids and vapours at magmatic-hydrothermal conditions.

Recent experimental and fluid/melt inclusion studies has pointed to hydrosilicate liquids as potential transporting media for some metals, like Ta, Cr, or Cu, and alkalis (e.g. Kamenetsky & Kamenetsky 2010; Smirnov *et al.* 2012; Borisova *et al.* 2012*c*; references therein). Such liquids, having gel-like properties, are composed mostly of silica, water, and NaOH; they may form at the magmatic-hydrothermal transition during late evolutionary stages in deeply evolved granite and pegmatite magmas and play a role in concentrating metals and affecting their distribution in hydrothermal-magmatic deposits. To what extent such media may influence the Au budget in natural systems remains to be verified by further analytical and experimental work.

#### Modelling

A major theoretical challenge in ore-deposit research on gold and accompanying metals will be interpretation of experimental data of solubility/ partitioning and metal speciation in the framework of physical-chemical equations of state, enabling predictions over the wide range of conditions of magmatic-hydrothermal Au deposits, from aqueous solution to hypersaline brine or low-density vapour phase. At present, accurate predictions for some Au species may only be done for the liquid and dense supercritical fluid phase (density  $>0.4 \text{ g/cm}^{\circ}$ ) using the HKF equation of state (e.g. Akinfiev & Zotov 2010). Generation of a self-consistent dataset within this model based on recent experimental data is awaited for several Au species, potentially important at magmatic conditions (e.g. Au chlorides, hydroxides, alkali metal-chloridesulphides, Zajacz et al. 2010). New models are currently under development attempting unified

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descriptions of the vapour-liquid region (e.g. Akinfiev & Diamond 2003), but they lack experimental data necessary for their parameterizing. Speciation and solubility data should be better integrated in user-friendly databases and computer codes allowing calculations of thermodynamics and kinetics of fluid-rock interactions (e.g. Oelkers *et al.* 2009).

In the last decade, molecular modelling approaches based on quantum chemistry and molecular dynamics have given new insights into atomic structure and hydration energy of ore metal complexes (e.g. Au, Cu, Ag), helping to interpret spectroscopic and solubility data and in making choices among possible speciation models to describe experimental data (e.g. Sherman 2010; Liu *et al.* 2011; Pokrovski *et al.* 2009*a, b,* 2013*a*). Such approaches, yet in their beginning, are expected to provide a direct link between the molecular properties of the dissolved species and their thermodynamic stability and solubility.

Another advance of the last decade is the growing application of physical hydrology approaches based on heat distribution and fluid flow models and permeability changes, which allowed integrated reactive transport models of fluid paths, pressure and temperature evolution, and three-dimensional ore distribution and shape (e.g. Driesner & Geiger 2007; Ingebritsen & Appold 2012; Weis et al. 2012). However, chemistry of fluid-rock interactions, mineral solubility, and chemical element speciation in the fluid phase are not yet quantitatively and systematically accounted for in these models, in particular, for trace elements like gold. Integration of chemistry and physics in the same conceptual model of ore deposit formation would, thus, be another major computational challenge, which can contribute both to our fundamental understanding of gold deposit formation and to improving gold ore exploration and extraction.

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