



# Solubility of gold in oxidized, sulfur-bearing fluids at 500–850 °C and 200–230 MPa: A synthetic fluid inclusion study

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## Abstract

Although Au solubility in magmatic-hydrothermal fluids has been investigated by numerous previous studies, there is a dearth of data on oxidized ( $\log fO_2 > FMQ+2.5$ ; FMQ – fayalite-magnetite-quartz buffer), sulfur-bearing fluids such as those that formed porphyry Cu-Au (-Mo) deposits. We performed experiments to constrain the effects of fluid salinity, HCl content, sulfur content,  $fO_2$  and temperature on Au solubility in such oxidized, sulfur-bearing fluids. For this purpose, small aliquots of fluids equilibrated with Au metal were trapped at high pressure and temperature in the form of synthetic fluid inclusions in quartz and were subsequently analyzed by LA-ICP-MS. Additionally, Raman spectra were collected from quartz-hosted fluid inclusions at up to 600 °C to help to identify the nature of dissolved gold and sulfur species. Gold solubility was found to be affected most strongly by the HCl content of the fluid, followed by  $fO_2$ , fluid salinity and temperature. Compared to these factors the sulfur content of the fluid has relatively little influence. At 600 °C and 100 MPa, fluids with geologically realistic HCl contents (~1.1 wt%) and salinities (7–50 wt% NaCl<sub>equiv</sub>) dissolve ~1000–3000 ppm Au at oxygen fugacities controlled by the magnetite-hematite buffer. At even more oxidized conditions (three log units above the hematite-magnetite  $fO_2$  buffer), HCl-, NaCl- and H<sub>2</sub>SO<sub>4</sub>-rich fluids can dissolve up to 5 wt% Au at 800 °C and 200 MPa. The observed Au solubility trends are controlled by HCl<sup>0</sup> species in the Na-H-Cl-SO<sub>4</sub> fluid and are quantitatively reproduced by existing thermodynamic data for Au-Cl complexes. In all experiments, AuCl<sup>0</sup> and AuCl<sub>2</sub><sup>-</sup> species are predicted to occur in comparable although variable concentrations, and account for more than 95% of Au solutes. Natural, high-temperature (>500 °C) brine inclusions from porphyry Cu-Au (-Mo) deposits contain significantly less Au than gold-saturated brines that were synthesized experimentally, implying that the natural brines were Au-undersaturated. Consequently, gold grades in Au-rich porphyries were not controlled by the precipitation of native Au, but rather by factors that caused the precipitation of Au-bearing hydrothermal sulfides such as bornite.

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## 1. INTRODUCTION

Gold is one of the most noble of all metals, existing dominantly as a native metal in the solid state and dissolving only scarcely into liquids or gases. However, the widespread occurrence of economic gold deposits that formed by hydrothermal processes (e.g., Kesler, 1994; Robb,

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2005) implies that gold transport and deposition by geological fluids is a common process in the Earth's crust. Therefore, knowledge of the factors that influence gold solubility in hydrothermal fluids is essential for understanding the formation of ore deposits.

Previous experimental studies on gold solubility in hydrothermal fluids focused either on relatively low temperatures (<500 °C) representative of epithermal environments (e.g., Zotov et al., 1989, 1991; Gibert et al., 1998; Pokrovski et al., 2009b; Kokh et al., 2016, 2017), on sulfur-free fluid systems (e.g., Frank et al., 2002; Stefansson and Seward, 2003; Hanley et al., 2005; Simon et al., 2005), or on fluids containing reduced sulfur species (e.g., Loucks and Mavrogenes, 1999; Tagirov et al., 2005; Simon et al., 2007; Zajacz et al., 2010). Loucks and Mavrogenes (1999) used synthetic fluid inclusions to investigate Au solubility in H<sub>2</sub>S-bearing fluids at 550–700 °C and 110–400 MPa. They observed solubilities up to 1000 ppm (by weight) Au and proposed AuHS(H<sub>2</sub>S)<sub>3</sub> as the dominant Au species. Subsequent studies on compositionally similar fluids identified Au(HS)<sub>2</sub><sup>-</sup>, Au(HS), Au(OH), Au(HS)H<sub>2</sub>S and/or Au<sup>(I)</sup> complexes with polysulfide as major Au species (Tagirov et al., 2005; Pokrovski et al., 2009b; Liu et al., 2011). Frank et al. (2002) investigated sulfur-free brines at 800 °C and 100 MPa and found that Au solubility increases with increasing HCl content, reaching 840 ppm Au at ~4.0 wt% HCl. They proposed HAuCl<sub>2</sub> as the dominant gold species. Simon et al. (2005, 2007) conducted experiments with NaCl-KCl-HCl-FeAsS fluids at 800 °C, 110–145 MPa and concluded that gold chloride complexes dominate both in sulfur-free and in (reduced) sulfur-bearing fluids. In contrast, Hanley et al. (2005) proposed Au(OH) as the dominant species in their salt-rich fluids at 600–800 °C, 150 MPa based on a negative correlation of Au solubility with fluid salinity. Most recently, Pokrovski et al. (2014, 2015) suggested an important role of the trisulfide ion (S<sub>3</sub><sup>-</sup>) in complexing gold, leading to Au solubilities up to ~6700 ppm in K<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-bearing fluids at 350 °C, 60 MPa. It should be noted that all these studies were carried at conditions in which sulfur occurs either in reduced state (S<sup>2-</sup>) or had a near-neutral valence (S<sub>3</sub><sup>-</sup>). However, evidence from porphyry Cu-Au (±Mo) deposits, which are one of our most important sources of Au (Kesler, 1994; Sillitoe, 2010), suggest that the ore-forming fluids in these deposits were highly oxidized – three to five log units above the fayalite-magnetite-quartz (FMQ) buffer (e.g., Burnham and Ohmoto, 1980; Hedenquist and Richards, 1998), where S<sup>4+</sup> or S<sup>6+</sup> (in SO<sub>2</sub> and sulfate, respectively) is the dominant sulfur valence (e.g., Binder and Keppler, 2011; Ni and Keppler, 2012). The present study thus aims at investigating gold solubility in oxidized (log *f*O<sub>2</sub> > FMQ+2.5), sulfur-bearing aqueous fluids similar to those responsible for porphyry Cu-Au (±Mo) formation.

## 2. METHODS

### 2.1. Experimental methods

We used synthetic fluid inclusions to trap fluids at high temperature and pressure and subsequently analyzed their

composition by LA-ICP-MS. Aqueous solutions containing various amounts of HCl, H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, LiCl, KCl, CsCl and MnCl<sub>2</sub> were prepared from analytical-grade chemicals and deionized water. Sodium chloride, and in two cases elemental sulfur, were added as solids. Quartz pieces of 1.0 × 1.6 × 10 mm size were cut from inclusion-free synthetic quartz in a way that their longest dimension was parallel to the *c*-axis of quartz crystal. The quartz pieces were then etched in concentrated hydrofluoric acid for about 1 h to form numerous etched channels, which favor the formation of large fluid inclusions during overgrowth of new quartz (Li and Audétat, 2009).

Three capsule setups were used in our experiments. In the first setup (Fig. 1a), gold capsules of 3.5 mm O.D. (outer diameter), 3.1 mm I.D. (inner diameter) and 20 mm length were loaded with a piece of etched quartz, ~40 mg solution, 0–16 mg of NaCl, 0–1 mg S, and a small SiO<sub>2</sub> glass rod (~4 mg). Run durations using this setup were kept short (10 h at 800 °C, 20 h at 700 °C; 40 h at 600 °C; 80 h at 500 °C), such that *f*O<sub>2</sub> was controlled by the starting materials rather than by the intrinsic *f*O<sub>2</sub> of the pressure vessel. In the second setup (Fig. 1b), which was used for runs #15, 28, 30, 33, 34, 48 and 49, the starting materials were contained in an inner Au or Au<sub>80</sub>Pd<sub>20</sub> capsule of 3.0 mm O.D., 2.7 mm I.D. and 20 mm length, which was then loaded with ~40 mg H<sub>2</sub>O and solid oxygen buffers – Re-ReO<sub>2</sub> (RRO), MnO-Mn<sub>3</sub>O<sub>4</sub> (MMO) or hematite-magnetite (HM) into an outer Au capsule (O. D. 4.6 mm; I.D. 4.3 mm; 35 mm length). Gold rather than Au<sub>80</sub>Pd<sub>20</sub> had to be used as inner capsules in the sulfur-bearing experiments because Au<sub>80</sub>Pd<sub>20</sub> was found to react with sulfur and to become very brittle during our procedure. In this setup, entrapment of fluid was initiated after 24–192 h by in-situ cracking, after which the runs were continued for another 24–120 h to allow for crack healing. However, in order to obtain larger fluid inclusions, the runs were started either with an etched quartz piece and a SiO<sub>2</sub> glass rod as in the previous capsule setup, or with a quartz piece that already contained large fluid inclusions that were pre-synthesized from H<sub>2</sub>O-KCl fluid. In both cases, already existing fluid inclusions were re-opened during the in-situ cracking, leading to distinctly larger fluid inclusions than if fluid inclusion-free quartz pieces were used (Li and Audétat, 2009). Fluid inclusions that were re-opened during in-situ cracking could be recognized by small fluid inclusion trails leading to them, and in the case of pre-synthesized ones by the absence of K-signals during LA-ICP-MS analysis. It is those re-opened inclusions that were preferentially chosen for LA-ICP-MS analysis (Li and Audétat, 2009). The third setup (Fig. 1c), which was used for runs #29, 38, 41 and 45, is similar to the setup b, except that an unetched quartz piece was used (to avoid fluid entrapment before Au solubility became low) and that the external nickel-nickel oxide (NNO) buffer was placed in an open Au capsule below the sample capsule instead of in a sealed outer capsule. The latter is possible because the material of the pressure vessel is very Ni-rich (~76 wt% Ni) and thus imposes a *f*O<sub>2</sub> that is already close to the NNO buffer. In all setups the sample-containing capsules were crimped, welded with a pulsed arc welder, then pre-shrunk at ~100 MPa H<sub>2</sub>O pressure, and finally weighed to check for potential leaks.

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