

The Stability of Group IB (Cu, Ag, Au) Metals in Water Vapour at Elevated Temperatures and Pressures

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It has been suggested that significant concentrations of copper, silver and gold may be transported by water vapour in natural hydrothermal systems (e.g., Hedenquist and Lowenstern, 1994). However, there have been very few experimental investigations of the solubility of these metals in water vapour at elevated temperatures and pressures. The high stability of chloride complexes of Group IB metals in aqueous solutions and the commonly high chlorinity of natural waters, suggest that such complexes may also play a role in metal transport by vapour. Support for this hypothesis is provided by the compositions of many natural vapours, notably those produced by passive volcanic degassing. For example, Gemmell (1987) reported copper, silver and gold concentrations in condensates from Momotombo volcano in Nicaragua of 0.4 to 8.4 ppm, 10 to 15 ppb, and 5 to 14 ppb, respectively (collected at temperatures of 450–886°C).

A number of researchers have used thermodynamic modeling to estimate metal concentrations in volcanic gases (e.g., Symonds and Reed, 1993). These models assumed that the behaviour of gaseous species can be described using component fugacities, but did not consider reactions between trace components dissolved in the gas and gas-solvent (i.e., water). However, in natural systems, water is the dominant gas solvent and omission of this phase could lead to unrealistic determinations of metal concentration. The aim of our study is to obtain experimental data on the behaviour of Group IB (Cu, Ag and Au) metals in the system Me-H₂O-HCl at temperatures from 300 to 360°C, and pressures up to 180 bars.

The experimental method employed is similar to that of Armellini and Tester (1993) for the NaCl system. Experiments were performed in titanium autoclaves that were loaded with quartz ampoules containing Ag or Cu chloride or native gold, a known mass of water, and HCl in quantities that yielded solutions with pH's of 1.5 to 5.0. Owing to the two possible oxidation states of Au at the experimental conditions, the oxygen fugacity was controlled by the assemblage MoO₂-MoO₃. Oxygen buffers were not required for the Ag and Cu chloride experiments. During experiments, care was taken to ensure that liquid saturation (water formation) did not occur. Initial experiments were conducted to determine equilibration times (8, 9, and 12 days for Cu, Ag and Au respectively).

The results of our experiments show that the presence of water vapour significantly increases the partial pressures of

CuCl, AgCl, and Au in HCl-bearing aqueous systems, relative to the water-free system. For example, the mole fractions of Ag are 7.2×10^{-10} and 1.27×10^{-8} at pressures close to water saturation and temperatures of 300 and 360°C, respectively. These mole fractions correspond to concentrations of 6 ppb and 100 ppb, respectively, and are at least 3–4 orders of magnitude higher than those predicted thermodynamically from volatility data (Tagirov *et al.*, 1993). The highest mole fractions obtained by us for Au correspond to concentrations in the vapour of 1100 ppb and 175 ppb at 300 and 360°C, respectively. Preliminary data for CuCl indicate copper concentrations of ~250 ppm in the vapour at 320 C and 75 to 100 bars.

The dominant gaseous species for Au, Ag, and Cu in chloride-bearing water vapour have a common Me:Cl stoichiometry of 1:1. Cu and Ag exhibit prograde solubility with temperature, whereas Au displays retrograde solubility. The Ag solubility data indicate that the metal atom is co-ordinated by 3 molecules of H₂O and 1 atom of Cl, whereas Au has variable co-ordination. At a temperature of 300 C, Au atoms are co-ordinated with 4 molecules of H₂O, at 340 C this co-ordination is 3-fold, and at 360 C the Au is in two-fold co-ordination. The Au:Cl ratio remains constant at 1:1. These hydration numbers are in good agreement with those predicted by *ab initio* calculations for silver, and also with experimentally derived data for aqueous silver solutions (Seward *et al.*, 1996). The hydration number for Cu (preliminary) is 4 at 320°C.

Prior to this study it was assumed that vapour transport of Group IB metals plays a relatively minor role in the formation of hydrothermal ore deposits. However, our study demonstrates that vapour can transport appreciable concentrations of these metals and that, in the case of copper and gold, the concentrations are sufficient to form ores.

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