Silver in geological fluids from in situ X-ray absorption spectroscopy and first-principles molecular dynamics

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Abstract

The molecular structure and stability of species formed by silver in aqueous saline solutions typical of hydrothermal settings were quantified using in situ X-ray absorption spectroscopy (XAS) measurements, quantum-chemical modeling of near-edge absorption spectra (XANES) and extended fine structure spectra (EXAFS), and first-principles molecular dynamics (FPMD). Results show that in nitrate-bearing acidic solutions to at least 200 °C, silver speciation is dominated by the hydrated Ag^+ cation surrounded by 4–6 water molecules in its nearest coordination shell with mean Ag–O distances of 2.32 ± 0.02 Å. In NaCl-bearing acidic aqueous solutions of total Cl concentration from 0.7 to 5.9 mol/kg H_2O (*m*) at temperatures from 200 to 450 °C and pressures to 750 bar, the dominant species are the di-chloride complex $AgCl_2^-$ with Ag–Cl distances of 2.40 ± 0.02 Å and Cl–Ag–Cl angle of $160 \pm 10°$, and the tri-chloride complex $AgCl_3^{2-}$ of a triangular structure and mean Ag–Cl distances of 2.60 ± 0.05 Å. With increasing temperature, the contribution of the tri-chloride species decreases from ~50% of total dissolved Ag in the most concentrated solution (5.9*m* Cl) at 200 °C to less than 10–20% at supercritical temperatures for all investigated solutions, so that $AgCl_2^-$ becomes by far the dominant Ag-bearing species at conditions typical of hydrothermal–magmatic fluids. Both di- and tri-chloride species exhibit outer-sphere interactions with the solvent as shown by the detection, using FPMD modeling, of H_2O, Cl^-, and Na^+ at distances of 3–4 Å from the silver atom. The species fractions derived from XAS and FPMD analyses, and total $AgCl_{(s)}$ solubilities, measured in situ in this work from the absorption edge height of XAS spectra, are in accord with thermodynamic predictions using the stability constants of $AgCl_2^-$ and $AgCl_3^{2-}$ from Akinfiev and Zotov (2001) and Zotov et al. (1995), respectively, which are based on extensive previous $AgCl_{(s)}$ solubility measurements. These data are thus recommended for chemical equilibrium calculations in mineral–fluid systems above 200 °C. In contrast, our data disagree with SUPCRT-based datasets for Ag–Cl species, which predict large fractions of high-order chloride species, $AgCl_3^{2-}$ and $AgCl_4^{3-}$ in high-temperature saline fluids. Comparisons of the structural and stability data of Ag–Cl species derived in this study with those of their Au and Cu analogs suggest that molecular-level differences amongst the chloride complexes such as geometry, dipole moment, distances, and resulting outer-sphere interactions with the solvent may account, at least partly, for the observed partitioning of Au, Ag and Cu in vapor–brine and fluid–melt systems. In hydrothermal environments dominated by fluid–rock interactions, the contrasting affinity of

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these metals for sulfur ligands and the differences both in chemistry and stability of their main solid phases (Ag sulfides, Cu–Fe sulfides, and native Au) largely control the concentration and distribution of these metals in their economic deposits.

1. INTRODUCTION

There is a growing need for better understanding the silver behavior in hydrothermal systems hosting a major part of Ag resources on Earth. Despite the low abundance of silver in the continental crust ($\sim$50 ppb, Rudnick and Gao, 2003), this trace element is enriched in hydrothermal fluids, with concentrations up to $\sim$100 ppm in brines as show fluid-inclusion analyses (e.g., Heinrich et al., 1999; Ulrich et al., 1999; Audédat et al., 2000; Borisova et al., 2012). Although silver usually follows its geochemical analogs, copper and gold, Ag/Cu and Ag/Au ratios in magmatic–hydrothermal deposits vary over 3–4 orders of magnitude. For example, typical Ag/Au mass ratios in porphyry deposits and epithermal adularia-quartz and alunite-quartz deposits, $\sim$1 ÷ 1000, are significantly higher than those of Carlin-type, skarn, and orogenic gold deposits, $\sim$0.001 ÷ 1 (e.g., Sillitoe and Hedenquist, 2003; Pal'yanova, 2008). Silver also fractionates from gold and copper in vapor–brine systems of magmatic–hydrothermal settings, where Ag partitions preferentially into the saline solution, whereas Au and partly Cu enrich the aqueous low-density vapor, as inferred from natural fluid inclusion data and laboratory experiments (Pokrovski et al., 2005a, 2008a; Kouzmanov and Pokrovski, 2013; references therein). Knowledge of the chemical speciation of silver in geological fluids over the range of magmatic–hydrothermal conditions is the primary requisite for modeling Ag transfers in natural vapor–fluid–melt systems, identifying favorable conditions of Ag-bearing minerals formation, and interpreting Ag tenors in different types of deposits. The present contribution is aimed to provide new data on the stoichiometry and structure of aqueous complexes that carry silver in hydrothermal fluids.

Among the three major natural ligands, hydroxide, sulfide, and chloride that transport base and precious metals in saline liquids and vapors, the Cl^- ion is believed to be the principal carrier of Ag, similarly to other base metals (Fe, Zn, Pb), as demonstrated by numerous experimental studies of Ag-bearing mineral solubilities and vapor–liquid and fluid–melt partitioning (e.g., Wood et al., 1987; Zotov et al., 1995; Wood and Samson, 1998; Pokrovski et al., 2005a, 2008a,b; Simon et al., 2008; references therein). The other two ligands, H_2S/HS^- and H_2O/OH^-, may contribute to Ag solubility only in fluids characterized by low temperatures and salinities, alkaline pH and/or elevated sulfide contents (e.g., Webster, 1986; Stefánsson and Seward, 2003; references therein). The effect of less common ligands such as ammonia (e.g., Wood and Samson, 1998), selenide (Akinfiev et al., 2008), bromide and iodide (Gammons and Yu, 2007), which may form strong chemical bonds with the Ag^+ ion, is expected to be weak in typical hydrothermal fluids with low concentrations of these components compared to the far more abundant chloride.

There is thus little doubt that chloride complexes play the major role in the hydrothermal and magmatic transport of Ag; however, they have been a subject of rather limited experimental work concerning the exact stoichiometry and thermodynamic stability of these important species. Two major sources of data on Ag–Cl aqueous species are those of Seward (1976) and Zotov et al. (1995, references therein) who carried out systematic measurements of native silver (Ag) and chlorargirite (AgCl) solubility over wide temperature (T), pressure (P) (to 450 °C and 1.5 kbar) and Cl concentration (to 7m NaCl and/or KCl) ranges. Their data indicate that the dichloride $AgCl_2^-$ is likely to be the dominant species to at least 2m Cl; the mono-chloride complex $AgCl^0$ is significant only in dilute solutions ($<$0.01m Cl); higher-order chloride complexes ($AgCl_3^{2-}$) form only in concentrated Cl brines at moderate temperatures. The large stability of $AgCl_2^-$ was confirmed by subsequent solubility work conducted in narrower T–P-composition windows (e.g., Gammons and Williams-Jones, 1995; Akinfiev and Zotov, 1999). Because the thermodynamic properties of the crystalline silver chloride, $AgCl_{(s)}$, and aqueous $AgCl_2^-$ were believed to be well constrained at $T \leqslant 300$ °C from those works, they were used indirectly to derive the formation constants of aqueous HCl^0 and chloride complexes of a number of metals like Zn, Ca, Mn, Pt, Pd, Nd by measuring changes in $AgCl_{(s)}$ solubility in the presence of the metal cation in moderately-saline solutions (Ruaya and Seward, 1986, 1987; Williams-Jones and Seward, 1989; Gammons, 1995; Gammons and Seward, 1996; Gammons et al., 1996; Tagirov et al., 1997).

However, large discrepancies exist on both stability and stoichiometry of Ag–Cl complexes at elevated salt concentrations ($>$2m) typical of natural magmatic–hydrothermal fluids. In particular, tri- and tetra-chloride complexes, which are known for silver at ambient temperatures (Martell et al., 2004) and for many other metals (Fe, Pb, Zn, Cd) both at ambient and hydrothermal conditions (e.g., Wood and Samson, 1998; Martell et al., 2004; Testemale et al., 2009; Bazarkina et al., 2010; references therein), were insufficiently explored for Ag above 100–200 °C. Based on the available solubility studies cited above and ambient-temperature data on [$AgCl_{1-4}$] complexes from abundant chemical literature (Martell et al., 2004; NIST Critical database 8.0; refs. therein), Sverjensky et al. (1997) and Akinfiev and Zotov (2001) have generated two independent datasets of thermodynamic properties of Ag–Cl complexes using the revised Helgeson–Kirkham–Flowers (HKF) model (Tanger and Helgeson, 1988). These datasets are now integrated in computer codes and largely used by geochemists; however, they appear surprisingly inconsistent as shown in Fig. 1. Calculations using these two datasets reveal large differences at $T > 300$ °C and $m_{Cl} > 1.5m$ in the Ag chloride species distribution dominated either by $AgCl_2^-$ (Akinfiev and Zotov, 2001) or $AgCl_4^{3-}$ (Sverjensky et al., 1997). This