The partitioning of Cu, Au and Mo between liquid and vapor at magmatic temperatures and its implications for the genesis of magmatic-hydrothermal ore deposits

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Abstract

The partition coefficients of Cu, Au and Mo between liquid and vapor were determined at $P = 130$ MPa and $T = 900$ °C, and $P = 90$ MPa and $T = 650$ °C and redox conditions favoring the dominance of reduced S species in the fluid. The experiments at 900 °C were conducted in rapid-quench Molybdenum-Hafnium Carbide externally-heated pressure vessel assemblies, whereas those at 650 °C were run in René41 pressure vessels. The fluids were sampled at run conditions using the synthetic fluid inclusion technique. The host quartz was fractured *in situ* during the experiments ensuring the entrapment of equilibrium fluids. A new method was developed to quantify the composition of the vapor inclusions from LA-ICPMS analyses relying on the use of boron as an internal standard, an element that fractionates between vapor and liquid to a very small degree. The bulk starting fluid compositions closely represented those expected to exsolve from felsic silicate melts in upper crustal magma reservoirs (0.64 m NaCl, 0.32 m KCl, ±0.2 m HCl and/or 4 wt% S). The experiments were conducted in $Au_{97}Cu_3$ alloy capsules allowing the simultaneous determination of apparent Au and Cu solubilities in the liquid and the vapor phase. Though the apparent metal solubilities were strongly affected by the addition of HCl and S in both phases, all three elements were found to preferentially partition to a liquid phase at all studied conditions with an increasing degree of preference for the liquid in the following order Au < Cu < Mo. The presence of HCl and S did not have a significant effect on the liquid/vapor partition coefficients of either Au or Cu, whereas the presence of HCl slightly shifted the partitioning of Mo in favor of the vapor. Ore metal partition coefficients normalized to that of Na ($K_{i-Na}^{liq/vap} = D_i^{liq/vap}/D_{Na}^{liq/vap}$) fall in the following ranges respectively for each studied metal: $K_{Au-Na}^{liq/vap} = 0.20 \pm 0.07$–$0.50 \pm 0.19$ (1σ); $K_{Cu-Na}^{liq/vap} = 0.36 \pm 0.12$–$0.76 \pm 0.22$; $K_{Mo-Na}^{liq/vap} = 0.67 \pm 0.15$–$2.5 \pm 0.8$. Decreasing T from 900 °C to 650 °C slightly shifted $K_{Au-Na}^{liq/vap}$ and $K_{Cu-Na}^{liq/vap}$ to the lower end of the reported ranges. A consequence of $K_{Au-Na}^{liq/vap}$ and $K_{Cu-Na}^{liq/vap}$ being significantly smaller than 1 is that much of the Au and a significant fraction of Cu may be carried to shallower levels of magmatic-hydrothermal systems by residual vapors despite potentially extensive brine condensation.
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1. INTRODUCTION

Magmatic-hydrothermal ore deposits serve as our primary resource of Cu and Mo, and are a major resource

of Au. The volatile phase exsolving from magmas due to decompression and crystallization is thought to be the major contributor to the metal and sulfur budget of these types of ore deposits (Hedenquist and Lowenstern, 1994; Richards, 2011). The magmatic volatile phase is known to contain significant concentrations of metal chlorides, HCl

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and various sulfur species (e.g. Holland, 1972; Candela, 1986; Williams et al., 1997; Frank et al., 2003; Webster, 2004; Zajacz et al., 2012, 2013). Indeed, aqueous fluids exsolving from dacitic to rhyolitic magmas are thought to contain several wt% dissolved metal chlorides based on the composition of magmatic fluid inclusions (Audetat and Pettke, 2003; Audetat et al., 2008; Zajacz et al., 2008) and the combination of experimental Cl partitioning data with the abundance of Cl in natural silicate melts (Shinohara et al., 1989; Kravchuk and Keppler, 1994; Botcharnikov et al., 2004; Webster, 2004; Wallace, 2005). The major chloride species in the magmatic volatile phase are $NaCl$, KCl, $FeCl_2$ and HCl with HCl/metal chloride ratios increasing with decreasing pressure and increasing melt peraluminosity (Baker et al., 1995; Williams et al., 1997; Frank et al., 2003; Simon et al., 2004; Zajacz et al., 2012). Various metal-chloride – H_2O systems are characterized by liquid/vapor immiscibility in the typical P-T range of upper crustal magma intrusions and related hydrothermal systems (Liebscher and Heinrich, 2007). Based on predicted salinities and typical P-T conditions of upper crustal magma intrusions, it is likely that some felsic systems exsolve co-existing vapor and liquid phases as evidenced by fluid inclusions in some natural systems (Audetat et al., 2008; Zajacz et al., 2008). Even if a single phase fluid exsolves from the magma originally, it will likely soon split into vapor and liquid due to decompression upon ascent (Bodnar et al., 1985; Heinrich, 2007). The liquid and vapor phase have rather different physical properties (i.e. density, surface wetting properties), and consequently, the liquid phase tends to stay in the deeper part of the hydrothermal system whereas the vapor phase rises to the shallower levels (Bodnar et al., 1985; Williams-Jones and Heinrich, 2005; Heinrich, 2007; Gruen et al., 2014). Provided that chemical fractionation occurs between vapor and liquid, various mineralization styles may be separated this way. Assemblages of co-existing vapor and brine inclusions in quartz veins from porphyry-type ore deposits indicated strong preferential partitioning of Cu, and occasionally Au into the vapor phase, and therefore, it was proposed that the vapors may play an essential role in the transfer of these metals to the site of mineralization (Heinrich et al., 1999, 2004; Heinrich, 2005; Williams-Jones and Heinrich, 2005; Hurtig and Williams-Jones, 2015). Preferential partitioning of these metals into the vapor phase in the presence of reduced S species was also supported by some experimental vapor/liquid partitioning data (Nagaseki and Hayashi, 2008; Pokrovski et al., 2008), whereas other studies, in particular those conducted at magmatic temperatures found Cu and Au partition into the brine (Simon et al., 2006; Frank et al., 2011). Recent studies have shown that the elevated Cu concentrations found in natural vapor inclusions are likely artefacts due to diffusive exchange of Cu^+ and other cations (i.e. H^+, Na^+) between the fluid inclusions and later-generation external hydrothermal fluids through the host quartz (Zajacz et al., 2009; Lerchbaumer and Audetat, 2012; Seo and Heinrich, 2013). Furthermore, experiments of Lerchbaumer and Audetat (2012) also identified preferential Cu partitioning into the liquid phase at

$T = 600–800\ °C$. Therefore, it seems likely that Cu preferentially partitions into the liquid phase over a broad range of P-T conditions. However, it still needs to be clarified to what extent the presence of H_2S and HCl may affect the liquid/vapor partition coefficient of Cu ($D_{Cu}^{liq/vap}$) at magmatic temperatures so that the efficiency of Cu transport by the vapor phase can be assessed.

Relative to Cu, Au shows much stronger preference to form complexes with reduced S species, which are thought to preferentially partition into the vapor phase (Benning and Seward, 1996; Archibald et al., 2001; Pokrovski et al., 2009a, b; Seo et al., 2009; Williams-Jones et al., 2009; Zajacz et al., 2010). Yet, alkali metal chlorides have also been shown to significantly affect the solubility of Au in reduced S-bearing magmatic vapors (Zajacz et al., 2010), and the latest studies have also highlighted the significance of trisulfur ions (S_3^-) in gold complexing in S-rich fluids (Pokrovski et al., 2015). Therefore, it is still unclear if at certain conditions Au may prefer the vapor over the liquid phase and the vapor may be the dominant transport media for Au in porphyry and related epithermal ore-forming systems (Seo and Heinrich, 2013).

To our knowledge, no experimental data exist on the liquid/vapor partitioning of molybdenum at magmatic and near magmatic temperatures. Fluid inclusions from natural systems indicate that Mo shows strong preference for the liquid phase (Ulrich et al., 1999; Audetat and Pettke, 2003; Klemm et al., 2007), which is consistent with Mo dissolution in the form of chloride, oxychloride or alkali molybdate complexes (Cao, 1989; Rempel et al., 2008; Ulrich and Mavrogenes, 2008). However, alternative, thio-molybdate complexes were proposed by Zhang et al. (2012), and such complexes could potentially increase Mo partitioning toward the vapor phase when reduced S species are present. In addition, Rempel et al. (2009) observed that Mo fractionates into the vapor in chloride-free systems at pH < 4, 300–370 °C at saturated water vapor pressure. Fluid/melt partitioning data obtained from assemblages of co-existing fluid and silicate melt inclusions have also indicated stronger Mo partitioning into lower-salinity fluids (Zajacz et al., 2008). Therefore, it is essential to clarify the role of HCl/alkali chloride ratios and the presence of reduced S on $D_{Mo}^{liq/vap}$.

Here we present experimentally determined liquid/vapor partition coefficients for Cu, Au and Mo within the P-T range where magmas are likely to produce chloride-rich fluids. We systematically investigated the effect of temperature and the addition of HCl and/or reduced sulfur species on the liquid/vapor partition coefficients. To be able to obtain these data, we developed a new experimental methodology that allows the determination of the salinity of HCl- and H_2S-rich vapor inclusions and, therefore, the quantification of their composition from LA-ICPMS analysis. In addition, our methodology allowed the simultaneous determination of how the apparent solubility of Au and Cu changes with fluid composition and temperature, which assisted the interpretation of the observed systematics in liquid/vapor partition coefficients.