Cu-Mo partitioning between felsic melts and saline-aqueous fluids as a function of $X_{\text{NaCleq}}$, $f_{O_2}$, and $f_{S_2}$

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ABSTRACT

The formation of porphyry Cu-Mo deposits hinges critically on the ability of an exsolving magmatic volatile phases (MVP) to efficiently extract the available Cu and Mo from the silicate melt and transport them to the site of mineralization. There has been substantial debate about the relative importance of the critical parameters likely to control metal partitioning among silicate melts and supercritical fluids, vapors, and brines. To explore the relative contributions of key MVP parameters ($X_{\text{NaCleq}}$, $f_{O_2}$, $f_{S_2}$), we present felsic magmatic Cu-Mo partitioning experiments at both reduced ($f_{O_2} = \text{NNO}+0.6$) and oxidized conditions ($f_{O_2} = \text{NNO}+2$), at high $f_{S_2}$, and over the full range of salinities ($X_{\text{NaCleq}}$) relevant to porphyry deposit formation. The experiments demonstrate that fluid-melt Cu partition coefficients ($D_{\text{Cu}}^{f/m}$) have a dominantly second-order exponential relationship with $X_{\text{NaCleq}}$ at relevant salinities, consistent with a (Na,K)CuCl$_2$ ion-pair complexation mechanism. We find a strong linear dependence of Cu partitioning on Cl partitioning between coexisting brine and vapor, in good agreement with limited data from unmodified natural fluid inclusions. Whereas H$_2$S can increase Cu partitioning via (Na,K)CuClCl(HS) formation, SO$_2$ has no measurable effect on Cu partitioning. These data allow for quantifying the strong partitioning of Cu out of silicate melts at MVP salinities above ~5 wt%, which will become further enriched into tardo-magmatic brines on phase separation. Our data also highlight that low-salinity (<2–3 wt% NaCl eq) oxidized MVPs are not capable of substantially extracting Cu from evolved silicate melts or transporting it to the site of mineralization. We also show that $D_{\text{Cu}}^{f/m}$ is a linear function of $X_{\text{NaCleq}}$ consistent with mono-chloride (e.g., {Na,K}MoO$_3$Cl), Na-K molybdate (e.g., {Na,K}HMoO$_4$), or thio-molybdate ( {Na,K}HMoO$_4$S$_2$) complexation mechanisms at modest salinities (>3 wt%) rather than the Mo-oxy-hydroxy [MoO$_4$(OH)$_2$] complexation observed at lower salinities. The $f_{S_2}$ of the magmatic system has a subordinate effect on $D_{\text{Cu}}^{f/m}$, with enhanced partitioning at higher $f_{S_2}$.

We use the combined data set to produce expressions for $D_{\text{Cu}}^{f/m}$ and $D_{\text{Mo}}^{f/m}$ as functions of $X_{\text{NaCleq}}$, $X_{\text{HYS}}$, and $f_{O_2}$.

$$
D_{\text{Cu}}^{f/m} = 8.0(\pm1.4) \times 10^4 \left(\frac{X_{\text{NaCleq}}}{X_{\text{HYS}}}\right)^{1.42} (1 + 180(\pm60)(X_{\text{HYS}})) + 380(\pm50)(X_{\text{NaCleq}}) + 0.8(\pm0.5)$$

$$
D_{\text{Mo}}^{f/m} \text{ (at NNO+2)} = 430(\pm60) \left(\frac{X_{\text{NaCleq}}}{X_{\text{HYS}}}\right) + 1.5(\pm0.7) \left(\frac{X_{\text{HYS}}}{X_{\text{NaCleq}}}\right).
$$

These equations provide Cu-Mo fluid-melt partition coefficients for common arc melt-MVP assemblages as their composition evolves through time and space. Quantitative modeling of the contrasting partitioning behavior of Cu and Mo using these equations will allow for significant improvement in understanding metal extraction and porphyry deposit formation.

Keywords: Experimental petrology, copper, molybdenum, magma, fluid phase, porphyry, partitioning, salinity, From magmas to ore deposits

INTRODUCTION

A critical step in the formation of porphyry-style ore deposits is the efficient extraction of ore metals (e.g., Cu, Mo, Au, Ag) from arc magmas during exsolution of magmatic volatile phases (MVPs)$^1$. These volatile phases represent the precursor or “proto-ore fluids” that must leave the magmatic hearth, enter fluid-focusing zones and react with other volatile phases and host rock to eventually generate the hydrothermally altered, hypogene sulfide ore zones characteristic of porphyry deposits (e.g., Sillitoe 2010; Sinclair 2007). Advances in magmatic-hydrothermal experiments and techniques for fluid inclusion analysis have enhanced our understanding of the physical and chemical properties of these MVPs and their influence on the extraction of different metals. Those experiments have focused on increasingly challenging aspects of simulating volatile partitioning, specifically the role of salinity (Candela and Holland 1984; Williams et al. 1995), the impact of the sulfur and $f_{S_2}$ (Frank et al. 2011; Simon et al. 2006), the role of CO$_2$ (Tattitch et al. 2015), and thermodynamic modeling of the complexes, which control metal speciation in high-temperature fluids (Mei

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$^1$This process is often referred to informally as “degassing” in the petrological literature. We use the two terms interchangeably here.

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