Cu-Mo partitioning between felsic melts and saline-aqueous fluids as a function of X_{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_{NaCleq}, f_{O_2}, f_{S_2}), we present felsic magmatic Cu-Mo partitioning experiments at both reduced (f_{O_2} = NNO+0.6) and oxidized conditions (f_{O_2} = NNO+2), at high f_{S_2}, and over the full range of salinities (X_{NaCleq}) relevant to porphyry deposit formation. The experiments demonstrate that fluid-melt Cu partition coefficients ($D_{\text{Cu}}^{\text{f/m}}$) have a dominantly second-order exponential relationship with X_{NaCleq} at relevant salinities, consistent with a $(\text{Na,K})\text{CuCl}_2$ 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_2S can increase Cu partitioning via $(\text{Na,K})\text{CuCl}(\text{HS})$ formation, SO_2 has no measureable 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$_{\text{eq}}$) 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 $D_{\text{Mo}}^{\text{f/m}}$ is a linear function of X_{NaCleq}, consistent with mono-chloride (e.g., $\{\text{Na,K}\}\text{MoO}_3\text{Cl}$), Na-K molybdate (e.g., $\{\text{Na,K}\}\text{HMoO}_4$), or thio-molybdate ($\{\text{Na,K}\}\text{HMoO}_2\text{S}_2$) complexation mechanisms at modest salinities (>3 wt%) rather than the Mo-oxy-hydroxy [$\text{MoO}_2(\text{OH})_2$] complexation observed at lower salinities. The f_{O_2} of the magmatic system has a subordinate effect on $D_{\text{Mo}}^{\text{f/m}}$, with enhanced partitioning at higher f_{O_2}.

We use the combined data set to produce expressions for $D_{\text{Cu}}^{\text{f/m}}$ and $D_{\text{Mo}}^{\text{f/m}}$ as functions of X_{NaCleq}, $X_{\text{H}_2\text{S}}$, and f_{O_2}

$$D_{\text{Cu}}^{\text{f/m}} = 8.0(\pm 1.4) \times 10^4 \left[(X_{\text{NaCleq}})^2 (X_{\text{H}_2\text{O}})^{14\pm 2} \{1 + 180(\pm 60)(X_{\text{H}_2\text{S}})\} \right] + 380(\pm 50)(X_{\text{NaCleq}}) + 0.8(\pm 0.5)$$
$$D_{\text{Mo}}^{\text{f/m}} \text{ (at NNO+2)} = 430(\pm 60) \cdot (X_{\text{NaCleq}}) + 1.5(\pm 0.7) \cdot (X_{\text{H}_2\text{O}}).$$

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