Cu-Mo-Au Partitioning and Ore Mineral Solubility: Constraints on the Role of Temperature, Pressure, and Volatile Fugacities

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The complex conditions under which volatile phases are exsolved from arc magmas play a key role in the formation of Porphyry Copper Deposits (PCD). Specifically, the efficiency by which ore metals are removed from melts by these "proto-ore fluids", metal ratios in the fluid(s), the mass of metals available for transport, and ultimately deposit grades are affected by several key intensive variables and volatile fugacitites. Previous experiments have shown that fluid salinity [1] as well as sulfur content [2] can strongly affect the ore metal partitioning. In addition, more subtle parameters such as cation ratios (e.g Na/K/H – [3]) along with melt ASI and $f\mathrm{H_2S}/f\mathrm{SO_2}$, may influence both Cu and Au. We present experiments designed to constrain the role of key variables (T, P, $f\mathrm{O_2}$, $f\mathrm{H_2S}$, $f\mathrm{SO_2}$, $\sum \mathrm{Cl}^v$) in influencing metal partitioning on a suite of ore metals in equilibrium.

In order to simulate complex, natural proto-ore fluids, we have performed $\mathrm{CuFeS_2}$-$\mathrm{MoS_2}$ saturated, Cu-Au-Mo-Re partitioning experiments using pumice from the Cardones Ignimbrite in northern Chile. These experiments examine fluid-melt-crystal partitioning and ore mineral solubility for a magmatic system similar to those found in major PCD. Experiments were performed at 100 & 200 MPa and super-solidus conditions (810 oC) in oxidized (NNO + 2) and reduced (NNO + 0.75) environments with respect to sulphur, as well as at near-solidus conditions (740 oC and NNO + 0.75). Observed Cu concentrations are consistent with Cl-dependent partitioning, modified by the presence of sulfur. The vapour/melt partitioning of Cu is enhanced by increased $f\mathrm{H_2S}$ at reduced conditions at 810 ^{o}C, but returns to Cl-dependence for high $f\mathrm{SO_2}$ at oxidized conditions ($\mathrm{D}_{Cu}^{v/m}$ decreases from 40 $\pm$ 20 to 10 $\pm$ 5). In contrast, molybdenum partitioning remains constant with changing $f\mathrm{O_2}$ ($\mathrm{D}_{Mo}^{v/m}$ = 3 $\pm$ 1 and 4 $\pm$ 2 respectively). This corresponds to a change in the vapour Cu/Mo ratio from $\sim$40:1 down to $\sim$1:1. The decrease in $\mathrm{D}_{Cu}^{v/m}$ is likely a result of the changes to available ligands in an $\mathrm{H_2S}$ dominated fluid compared to an $\mathrm{SO_2}$ dominated fluid. The effect of oxidation may be stronger for Cu relative to Au as the Cu/Au ratio in the vapour drops from $\sim$100:1 down to $\sim$30:1 at higher $f\mathrm{O_2}$. At 740 ^{o}C, near the solidus for the Cardones, the solubility of Mo in the silicate melt is much lower, indicating that temperature and/or melt properties will exert a strong control on Mo availability during volatile exsolution. Supercritical experiments (200 MPa) have recently been completed to evaluate ore-mineral solubility, and the influence of T and $f\mathrm{O_2}$, for fluids of median salinity compared to vapours and brines at 100MPa. Evaluating changes to ore metal ratios (Cu/Mo, Cu/Au, Mo/Re etc.) will allow us to evaluate complex ore metal behaviour during the progression of magmatic volatiles from deep one-phase systems, through fluid unmixing, continued exsolution down to the solidus, and finally sub-solidus transport and deposition.

References:

[1] Candela and Holland (1984) GCA, 48, 373-380

[2] Simon et al. (2006) GCA, 70, 5583-5600

[3] Zajacz et al. (2011) GCA, 75, 2811-2827